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Photographie de la couverture - Équipe d'intervention que prend des mesures a un entrepôt de produits chimique détuit par le feu a Grand Coulee Saskatchewan

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MEMBRANE-BASED PROCESSES FOR THE TREATMENT OF SPILLED WOOD PRESERVING SOLUTIONS

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INTRODUCTION

This paper illustrates ways in which membrane technologies can be used alone or in combination with other conventional treatment technologies for the treatment of spilled wood preserving solutions.

The technologies discussed in case history form in this paper include **reverse osmosis** and **ion exchange** for recovery and reuse of spilled copper-chrome-arsenic wood treating solutions as well as **reverse osmosis** and **nanofiltration** along with **granular activated carbon** for the treatment of pentachlorophenol contaminated groundwater. In addition, this paper discusses the potential use of **membrane/biological** treatment for the treatment of pentachlorophenol contaminated groundwater.

Each of these applications is discussed separately in the following sections.

CASE 1 RECOVERY AND REUSE OF SPILLED WOOD TREATING SOLUTIONS BY RO/IX

Background

Wood can be treated with chromated copper arsenate (CCA) to reduce biodegradation and extend the wood's useful life. These treating chemicals are effective because of their toxicity to wood degrading organisms, but they are also toxic to aquatic organisms. For this reason, care must be taken to prevent negative environmental impacts as a result of accidental spills or improper handling of these wood treating chemicals.

In 1989 a fire at the B.C. Clean Wood wood treating plant in Surrey, British Columbia, resulted in the accidental spill of wood treating solution containing 3% CCA along with an organic-based wood dye. These two solutions combined with firefighting effluents and rain water to produce in excess of 380 m^3 (100,000 US gallons) of wastewater. The wastewater was contained on-site in ditches, portable pools, and tanker trucks. The British Columbia Ministry of Environment ordered treatment of this wastewater prior to discharging it to the nearby Fraser river.

Within two days of request, a reverse osmosis/ion exchange (RO/IX) system, designed and built by ZENON, was sent to the spill site in B.C from another wood preserving plant site (in the U.S.),. The suitability of RO/IX treatment for this type of application had already been demonstrated as a result of earlier work by ZENON involving the treatment of CCA contaminated groundwaters.

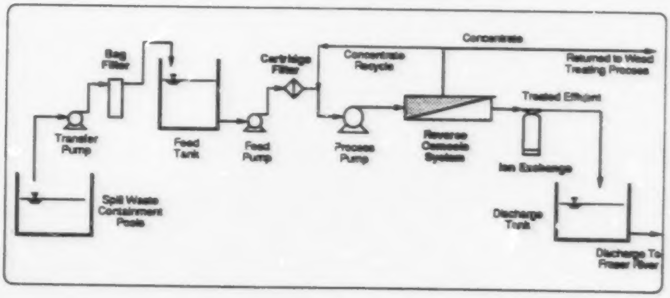
The following sections describe the treatment approach and results of the on-site cleanup which was aimed at meeting the B.C. MOE requirements for effluent quality prior to discharge, while at the same time, maximizing the extent to which contaminants could be recovered for reuse in the wood treatment process.

Process Description

Three treatment stages were used for the cleanup process: prefiltration, reverse osmosis (RO), and ion exchange (IX). A schematic of this treatment system is illustrated in Figure 1. Each stage of the treatment system served the purpose of removing specific components in the waste stream.

The prefiltration stage removed suspended solids from the wastewater. The wastewater was pumped from on-site containment pools through a 25 µm bagfilter, followed by a 5 µm cartridge filter prior to the RO treatment stage. The removal of suspended solids from the waste is critical to the operation of the RO system, particularly when using a spiral wound RO membrane module design.

Figure 1 - Flow Schematic of Cleanup Operation


Concentrate
Bag Filter
Cartridge Filter
Concentrate Recycle
Returned to Wood Treating Process
Treated Effluent
Transfer Pump
Feed Tank
Feed Pump
Process Pump
Reverse Osmosis System
Ion Exchange
Spill Waste Containment Pools
Discharge Tank
Discharge To Fraser River

The RO stage is the main component of the treatment train and was used to remove most of the dissolved metal (CCA) and organic contaminants in the waste stream. The RO stage employs a high pressure process pump to pass waste across the surface of a selective reverse osmosis membrane. The membrane permits the passage of water. The dissolved contaminants are rejected. Eight spiral membrane modules, representing 63 m^2 (680 ft^2) of membrane area, were operating at an average applied pressure of approximately 2760 kPa (400 psi). The membrane bank separated the feed stream into an RO concentrate stream (membrane reject) and an RO permeate stream. Part of the RO concentrate was recycled back to the process pump in order to maintain a desired volume recovery (percentage of feed volume recovered as permeate) and the remainder was returned to the wood treating process for reuse. The RO permeate was directed to the IX polishing stage for additional metals treatment.

The IX stage removed most of the remaining metal ions from the RO permeate. This stage consisted of two 35 L (1.2 ft^3) anion resins beds connected in parallel, followed by one 100 L (3.5 ft^3) cationic resin bed connected in series. The anion resins removed negatively charged ions (e.g. AsO_4^{3-} and CrO_4^{2-}) from the RO permeate, and the cationic resins removed positively charged ions (e.g. Cu^{2+}). Effluent from the IX stage was extremely low in metals. The effluent was stored in 40 m^3 (10,000 US gallon) tanks and was monitored by the MOE prior to discharge to the Fraser river.

The prefiltration stage required the replacement of the bagfilter and cartridge filter each operating day. These spent filters were disposed of off site as solid hazardous waste. The RO membranes required daily cleaning due to materials in the incoming feed stream fouling the membranes and causing a decrease in permeate productivity. Cleaning was done by circulating specially formulated proprietary cleaning agents (designated MC-1 and MC-4) through the RO system for 1.5 to 2.0 hours each cleaning cycle. The MC-1 cleaner is acid based and is designed to remove inorganic foulants, and the MC-4 cleaner is caustic/detergent based and is designed to remove organic foulants. Regular maintenance of the prefilters and RO membranes ensured optimal treatment performance.

Process Performance

During the first 5 days of on-site operation, ZENON trained B.C. Clean Wood staff on the proper operation and maintenance of the system. Daily operation and monitoring was then turned over to B.C. Clean Wood, and the remaining weeks of cleanup were managed through ZENON's central office in Burlington, Ontario. The treatment system remained on-site for a total of three weeks and successfully treated 340 m^3 (90,000 US gallons) of waste.

During the three weeks on-site, the treatment system was operated 24 hours a day and 5 days a week and resulted in the production of 100 m^3 (27,000 US gallons) of RO concentrate and 240 m^3 (63,000 gallons) of treated effluent. The RO concentrate plus the smaller volume of spent cleaning solutions were returned to B.C. Clean Wood's plant and was successfully reused as makeup water for their wood treating operation. The treated effluent was checked regularly by the MOE and was deemed suitable for discharge to the Fraser river. The treatment system was closely monitored throughout the cleanup operation, to ensure optimal operability, and exceeded expectations for both effluent quality and productivity.

A summary of analytical results from the treatment operation is shown in Tables 1 and 2. The sample content of copper (Cu), chromium (Cr), and arsenic (As) was analyzed by the Inductively Coupled Argon Plasma (ICAP) method, and the presence of organic wood dye was measured based on total organic carbon (TOC). The feed stream appeared dark and turbid throughout the entire cleanup operation. The dark colour was attributed to wood dye and the turbidity from suspended material picked up during waste collection. Although no suspended solids analyses are reported, the visual presence of suspended solids was very low after passing the waste through the prefiltration stage, and was not visually detectable in the RO permeate.

Table 1
Summary of Chemical Analysis

Sample Stream	Chromium mg/L	Copper mg/L	Arsenic mg/L	TOC mg/L
RO Feed	40.0	5.15	24.4	33*
RO Concentrate	90.8	22.4	57.7	n/a
RO Permeate	0.36	0.008	0.039	n/a
Ion Exchange	0.003	0.004	0.025	17.0
Discharge Tank	0.033	0.006	0.023	n/a
RO % Removal	99.1%	99.8%	99.8%	n/a
IX % Removal	>99.9%	>99.9%	99.9%	48%

* Estimated

The percent removal of contaminants is also shown in Table 1. The removal is based on measured concentrations of contaminants in the RO permeate and IX effluent as compared to the RO feed. The RO stage was the key component of the treatment system, as can be seen by the >99% removal of Cu, Cr, and As in the feed stream. Post treatment with IX further reduced these metal concentrations to below the 0.05 mg/L drinking water discharge guideline, increasing removals to >99.9%. The overall percent removal of organic contaminants by the system is estimated at 48%. This removal is lower than anticipated based on the fact that the dye colouring present in the feed was not visible in the treated effluent. Unfortunately TOC analyses were not available for the RO feed stream, and best estimates of TOC in the feed may be somewhat lower than actual. In any case, the overall removal of contaminants from the waste stream was more than enough to meet the British Columbia MOE's criteria and, as a result, the MOE pronounced the treatment system effluent suitable for discharge to the Fraser River.

Table 2
Effluent Quality Comparison

Element Analyzed	Waste Influent mg/L	Treated Effluent mg/L	Vancouver Tap Water mg/L
Phosphorus	0.7	< 0.01	< 0.01
Arsenic	23.9	< 0.04	< 0.04
Lead	< 0.005	< 0.005	< 0.005
Cobalt	< 0.004	< 0.004	< 0.004
Barium	0.04	< 0.004	< 0.004
Chromium	34.7	< 0.001	< 0.001
Copper	11.5	< 0.002	1.2
Aluminum	0.6	< 0.01	0.09
Magnesium	3.6	< 0.01	0.15
Strontium	0.1	< 0.002	0.07
Molybdenum	0.01	< 0.001	< 0.001
Cadmium	< 0.001	< 0.001	< 0.001
Nickel	<0.02	< 0.002	< 0.002
Manganese	0.57	< 0.001	0.01
Vanadium	< 0.001	< 0.001	< 0.001
Zinc	1.2	< 0.002	0.05
Iron	0.79	< 0.002	0.07
Calcium	29.3	< 0.01	1.4

The productivity controlling component of the treatment system is the RO stage. The productivity of this stage is measured as the volume rate of membrane permeate divided by the available membrane area in the system, and is represented by the flux unit L/m^2•h (LMH) or gal/ft^2•day (gfd). The membrane flux gradually decreased from 34 LMH (20 gfd) to 11.9 LMH (7 gfd), over the first 200 hours of operation, and then became relatively stable at 11.9 LMH for the final 100 hours of operation. The estimate average rate of permeate and concentrate volume rate of productivity from the RO system throughout the operation is 13.2 L/m (3.5 gpm) and 5.7 L/m (1.5 gpm), respectively.

Membrane cleaning with MC-4 was employed at least every 24 hours to deal with flux reduction due to membrane fouling. Although cleanings were obviously helping to restore some of the flux lost, they did not prevent the gradual flux decline to a plateau of 11.9 LMH (7gfd). It is surmised that the MC-4 wash was removing some form of foulant material (reversible foulants) during cleaning, but other forms of foulant material (irreversible foulants) were remaining on the membrane surface. The irreversible foulants decrease flux in two ways: 1) they decreased the available membrane pore area for water permeation and 2) they changed the surface chemistry of the membrane to a more hydrophobic nature and thus repelling water. Although the foulants reduced membrane flux, membrane permeate quality remained constant throughout the operation.

Following the return of the system to ZENON, a special organic membrane cleaner was used in an attempt to remove the foulants affecting flux. The in-house cleaning appeared to remove much of the fouling materials, based on the 25.5 LMH (15 gfd) final flux (on water) compared to the 34 LMH (20 gfd) starting flux (on water) - a 75% flux restoration. Although this cleaning could have been regularly employed in the field, it was not considered efficient or economical to do so in view of the relatively short term duration of the clean up operation. What is important to note however, is the membranes could be cleaned at the end of the waste treatment operation thus enabling them to be reused for similar applications in the future.

The performance of the RO/IX treatment system was highly successful. The system was able to achieve and maintain a high quality treated effluent even when encountering changes in feed concentration and fluctuations in productivity. The skid mounted treatment system facilitated rapid commissioning and decommissioning, and its simplicity enabled routine daily operation to be conducted by the client. The results of this cleanup operation demonstrate the potential for RO/IX treatment in spills of this nature, as well as other wastewater streams containing low concentration of organic and inorganic contaminants particularly where there is an opportunity to reuse the recovered concentrates.

Economics

The cost of treating the 380 m^3 (90,000 US gal) of wastewater was in the order of 0.08 ¢/L ($0.32/gallon). This excludes credits for the recovered CCA concentrates which were returned to the wood treating process. The only residues which required off-site disposal were the spent bags and cartridges from the RO system prefilters. The breakdown of costs is as follows:

Labour	$10,500
Equipment transportation and rental	9,500
Analysis	1,500
Membrane cleaners	1,000
IX resins	3,000
Bag filters	3,000
Total Cost	$28,500

Conclusions

Results of the B.C. Clean Wood spill cleanup and related testing of the treatability of CCA contaminated groundwaters from other wood treating sites have lead to the following conclusions:

- RO/IX has been demonstrated as an effective treatment method for removing >99.9% of feed CCA contaminants to a discharge level of less than 0.05 mg/L. In addition, the system was capable of removing virtually all colour associated with organic based wood dyes. This performance resulted in meeting the goal of treating 340 m^3 (90,000 US gallons) of waste to a level suitable for discharge to the Fraser River.

- The RO concentrate produced by the process is suitable for direct reuse in the wood treating process.

- RO membrane cleaners and IX regenerants have also been demonstrated to be suitable for reuse in the wood treating process. Therefore, the only residues which required off-site disposal from this process were spent prefilter bags and cartridges.

- Foulants in the waste feed stream caused membrane productivity rates to drop by 60% before stabilizing. However, a special in-house cleaning resulted in a 75% flux restoration and the potential for reusing the membranes.

- A skid mounted RO/IX system can be rapidly commissioned on a spill site and safely operated by the client with minimal supervision.

- The RO/IX waste treatment system indicates significant potential for wood treating spill cleanups and other wastewater streams containing low concentrations of organic and inorganic contaminants.

CASE 2 REMOVAL OF PENTACHLOROPHENOL FROM GROUNDWATER USING RO/NF AND GAC

Introduction

ZENON Environmental Inc. was contracted by a major wood preservative company in the US to recommend a potential solution for removing PCP from the contaminated groundwater and to conduct in-house treatability studies aimed at confirming the feasibility of the recommended treatment process. The spillage of wood preservatives over the years at one of their sites has led to significant levels of PCP and fuel grade oil in the surrounding groundwater supply. Reverse osmosis (RO) following by activated carbon adsorption was the process selected for treatability testing.

RO has been successfully applied for removing PCP concentrations of up to 2,200 ppm (Whittaker and Straforelli, 1984). Rejections greater than 99.8% were reported for feeds containing 156 ppm to 1,900 ppm. Polishing of the permeate stream was carried out with granular activated carbon (GAC) to reduce PCP levels below 125 ppb. It was felt that PCP levels could be reduced below 1 ppb in the groundwater with RO/GAC treatment provided adequate pretreatment measures were taken to reduce free and emulsified oil in the feed below 10 ppm.

Test Procedures

Pretreatment

The two 55 gallon samples received for testing contained significant levels of free and emulsified oil. Each drum had a layer of free oil about 10 mm in depth lying above the aqueous phase. The pretreatment procedure first involved a settling period of 2 days to allow gravity separation of the oil and aqueous phases. Equal volumes of the aqueous phase from each sample drum were then pumped into a 500 L holding tank and blended together to form a 50/50 composite sample for carrying out treatability tests. Prior to RO treatment, the composite sample was pumped through two 5 micron cartridge filters in series to remove suspended solids, residual free oil and most of the emulsified oil. Samples of the combined aqueous phases were taken before and after prefiltration and submitted for oil/grease analysis. In addition, the sample taken before prefiltration was analysed for TSS, while the sample taken after filtration was analysed for TDS, total phenols, pentachlorophenol, metals and anions.

Reverse Osmosis Tests

The RO test system consisted of a 300 L feed tank, a 200 L permeate tank, a 4" x 40" FilmTec FT–SW30HR membrane, a heat exchanger to maintain a constant operating temperature, a high pressure pump and the necessary piping, fittings and gauges.

Two series of tests were conducted with this equipment. In the first set of tests, the RO system was operated in a recovery mode (i.e. permeate was recovered from the system and directed to a separate tank) to concentrate an initial feed volume of 380 L to recovery levels of 8%, 33%, 50%, 70%, 79% and 85% consecutively. A composite sample of all the permeate collected was submitted for TOC, pentachlorophenol, total phenols, metals and anions analyses.

A second series of tests were conducted with the concentrate after 85% recovery to determine the effect of feed pressure on membrane flux. The tests were all carried out in a stability mode to maintain a constant set of feed conditions. Permeate rates were measured with feed pressures of 300, 400, 500 and 600 psig.

Carbon Adsorption Tests

The permeate generated in the RO tests was used as the feed for activated carbon tests. A series of equilibrium adsorption tests were first performed to generate an adsorption isotherm for pentachlorophenol. A column test was then conducted to determine the breakthrough characteristics of PCP under dynamic operating conditions. Selected samples of the column effluent were submitted for PCP analysis by GC.

Results and Discussion

General

Analytical results from the treatability tests are presented in Table 1. Both total phenols and PCP analyses were done on the RO feed and permeate to give an indication of the fraction of phenolics other than PCP present in the samples. However, the total phenolic concentration reported in Table 1 for the RO feed was considerably lower than the pentachlorophenol concentration measured by GC suggesting that the 4-aminoantipyrine colorimetric method used for determining total phenols had a very poor response to PCP.

Table 1
Analytical Results for Treatability Tests

Parameter (mg/L)	Original Sample	After 5 µ Prefiltration	RO Permeate (85% Recovery)	GAC Column Effluent
pH	-	-	6.1	-
TSS	18	-	-	-
TDS	-	314	-	-
TOC	-	-	5	-
Oil & Grease	108	102	-	-
Total Phenols	-	0.08	< 0.05	-
Pentachlorophenol	-	5.1	0.052	0.00092
Fluoride	-	< 0.1	< 0.1	-
Chloride	-	21	< 0.2	-
Nitrite (as N)	-	< 0.2	< 0.2	-
Bromide	-	< 0.8	< 0.8	-
Nitrate (as N)	-	1	< 0.2	-
Phosphate (as P)	-	< 0.8	< 0.8	-
Sulfate	-	37	< 1	-
Calcium	-	77	0.48	-
Magnesium	-	20	< 0.05	-
Sodium	-	12	1.5	-
Potassium	-	3.6	< 0.5	-
Aluminum	-	< 0.03	< 0.03	-
Barium	-	0.055	< 0.002	-
Beryllium	-	< 0.001	< 0.001	-
Boron	-	0.32	0.13	-
Cadmium	-	< 0.002	< 0.002	-
Chromium	-	< 0.004	< 0.004	-
Cobalt	-	< 0.01	< 0.01	-
Copper	-	< 0.006	< 0.006	-
Iron	-	0.021	< 0.01	-
Lead	-	< 0.02	< 0.02	-
Manganese	-	1.4	< 0.005	-
Molybdenum	-	< 0.02	< 0.02	-
Nickel	-	< 0.01	< 0.01	-
Phosphorus	-	< 0.06	< 0.06	-
Silicon	-	8.3	< 0.05	-
Silver	-	< 0.01	< 0.01	-
Strontium	-	0.19	< 0.001	-
Sulphur	-	14	0.24	-
Thallium	-	< 0.08	< 0.06	-
Titanium	-	< 0.01	< 0.01	-
Vanadium	-	< 0.005	< 0.005	-
Zinc	-	0.013	< 0.005	-
Zirconium	-	< 0.01	< 0.01	-

The separation of free and emulsified oil from the aqueous phase in the pretreatment step resulted in a reduction of PCP levels from about 170 ppm to 5.1 ppm. In its undissociated state, PCP is fairly hydrophobic and hence will be more strongly absorbed by an oily phase than an aqueous medium. At the 6 to 7 pH range found in the groundwater, PCP is partially undissociated explaining the reduction in PCP concentration below its expected solubility of about 20 ppm. Since pH directly affects the distribution of dissociated and undissociated PCP in a wastewater, the pH of the groundwater will influence the amount of PCP remaining in the aqueous phase after pretreatment, and as such, decreasing the groundwater pH below the dissociation point will increase the amount of PCP removed in the oily phase.

Oil and grease analyses were performed on the aquoeus phase before and after prefiltration to determine the removal efficiency of the 5 micron filters and to indicate the loading capacity necessary for a continuous oil removal system. According to the analytical results, the oil and grease levels dropped by less than 6% after prefiltration although the brown colour of the water was dramatically reduced. The methylene chloride extraction method for oil and grease analysis is not only specific to free and emulsified oil but will also measure dissolved organics. Hence, the high oil and grease level remaining in the prefilter effluent may consist primarily of dissolved organics.

Reverse Osmosis Tests

The effects of system recovery and feed pressure on the membrane flux are illustrated in Figure 1 and 2 respectively. The data presented in these figures are tabulated in Table 2 and 3 along with the conditions under which the tests were performed.

Figure 1
Membrane Flux Versus Recovery

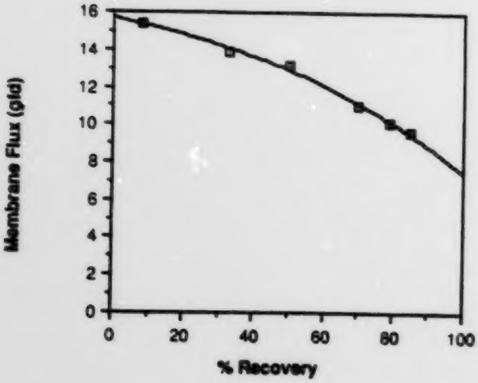


Figure 2
Membrane Flux Versus Feed Pressure

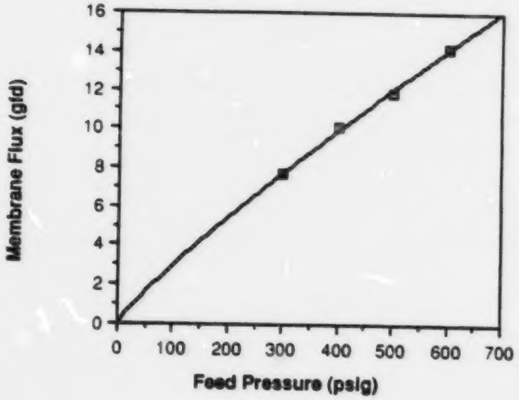


Table 2
Membrane Flux at Varying Recoveries

Run No.	% Recovery	Permeate Rate (gpm)	Membrane Flux (gfd)
1	8%	0.85	15.4
2	33%	0.77	13.9
3	50%	0.73	13.2
4	70%	0.61	11
5	79%	0.55	10.1
6	85%	0.53	9.6

Test Conditions: Operating Temperature = 72°F (22°C)
Feed Pressure = 400 psi
Feed Flowrate = 10 gpm

Table 3
Membrane Flux at Varying Feed Pressures

Run No.	Feed Pressure (psig)	Permeate Rate (gpm)	Membrane Flux (gfd)
1	300	0.42	7.7
2	400	0.55	10.1
3	500	0.65	11.8
4	600	0.78	14.2

Test Conditions: Operating Temperature = 74°F (23°C)
Feed Flowrate = 10 gpm
Recovery = 85%

Figure 1 shows a decrease in membrane flux as the recovery level is increased. This trend is characteristic of RO treatment and helps to determine the maximum recovery at which the process can be economically operated. Several factors may contribute to the decreasing flux at higher recoveries, but the increased osmotic pressure exerted by the concentrated feed and a higher degree of organic fouling are likely the most significant in this case. As the feed becomes more concentrated at increasing recoveries, emulsified oil remaining in the feed will tend to destabilize and foul the membrane surface. However, the data in Table 3 and Figure 2 indicates that a full-scale RO plant could likely operate at recoveries in excess of 85%, and still provide a reasonable degree of productivity in the order of 14 to 15 gfd provided that the RO was operated at pressures at approximately 600 psi.

PCP was 99% rejected by the RO membrane at an operating pressure of 400 psi, giving an average PCP concentration of 52 ppb in the permeate. In addition, metal and anion concentrations were virtually all reduced to undetectable levels (refer to Table 1).

A scale prediction program run on the feed's inorganic composition showed that there was no potential for calcium carbonate, calcium sulphate or strontium sulphate scaling at recoveries up to 95% as a result of the low concentrations of inorganics in the feed. However, some barium sulphate precipitation was predicted to occur at recoveries above 50%, so the RO feed will likely have to be dosed with a scale inhibitor.

Organic fouling of the membrane surface is also a concern in this application. At the completion of the RO testing, the membrane flux was measured on a demineralized tap water feed before and after cleaning the membrane with an alkaline cleaner. The flux increased from 15.3 gfd to 18.3 gfd after cleaning indicating that there was some organic fouling of the membrane. A flux of 18.3 gfd is still a bit low for a pure water feed and is possibly the result of incomplete removal of the organic foulant in the membrane cleaning process and/or a degree of irreversible fouling due to the conditioning of the membrane to the feed (i.e. alteration of the membrane surface chemistry).

Testing is required at the pilot scale to further assess the efficiency of pretreatment methods and to confirm design parameters for a full-scale RO unit. In addition, effective membrane cleaning procedures need to be evaluated to counteract potential organic fouling of the membranes.

Carbon Adsorption Tests

PCP levels were reduced below the 0.5 μg/L detectable limit in all the equilibrium adsorption tests performed. An isotherm therefore could not be constructed for PCP in the RO permeate since the analytical results were not finite values. In fact, it would be difficult to construct an accurate PCP isotherm for a feed containing only 52 ppb of PCP because of the very small carbon dosages that would have to be added and the sensitivity required for the PCP analyses. In this case, however, the information obtained in a column test is sufficient to size a full-scale carbon column.

As a result of the low permeate PCP concentrations, a large volume of permeate was needed to generate a PCP breakthrough profile from the GAC column. The column test was conducted for a total of 428 hours during which time 6,350 bed volume (BV) of permeate were passed through the column. All the remaining permeate was consumed at this point.

Effluent PCP concentrations are tabulated in Table 4 and plotted against bed volumes of column effluent collected in Figure 3. From the graph in Figure 3, it can be seen that the 1 ppb breakthrough point occurred after approximately 5,200 bed volumes. The composite PCP concentration was about 0.92 ppb after 6,350 bed volumes suggesting that at least 6,000 bed volumes of permeate can be treated before exceeding an average PCP concentration of 1 ppb. This corresponds to an operating adsorption capacity of 0.6 mg PCP/g carbon. A two column system is recommended to permit greater amounts of PC to be adsorbed unto the carbon bed before they are replaced.

Table 4
Results of Activated Carbon Column Test

Sample No.	Elapsed Time (hrs.)	Effluent Vol. Collected (BV)	Effluent PCP Concentration (ppb)
1	102	1520	0.03
2	202	2965	0.15
3	325	4798	0.41
4	379	5608	1.4
5	428	6350	5.1

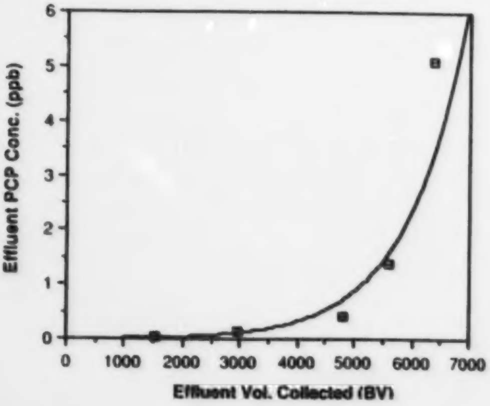
Operating Conditions:

Initial Feed PCP Concentration = 52 ppb
Feed Flow Rate = 10 ml/min (15 BV/h)
Bed Volume (BV) = 39 cm3
Bed Depth = 8 cm

Assessment of Alternative Treatment Options

Although the technical feasibility of the RO/GAC treatment process was confirmed for this particular groundwater sample, it may not be the most efficient means of removing PCP from all groundwater problem sites. Other treatment options need to be considered for both efficacy and economics before selecting an optimum process.

Figure 3
PCP Breakthrough Profile



The results of this treatability study indicate that activated carbon adsorption may be able to achieve the desired effluent quality without RO treatment. However, the pretreatment step will have to be more involved in order to reduce PCP levels below 1 ppm. The presence of significant levels of other dissolved organics (particularly the heavier aliphatic and aromatic hydrocarbons present in fuel grade oil) makes it difficult to accurately predict if GAC can reliably produce an effluent PCP concentration of <1 ppb due to competitive adsorption. Using GAC, Guo et al (1979) were only able to reduce PCP concentrations down to 20 ppb with a feed containing 0.44 ppm PCP and 54 ppm TOC.

Two possible methods of reducing PCP levels below 2 ppm in the pretreatment step are gravity settling/ultrafiltration or pH adjustment/gravity settling/oil coalescing. Depending on the free and emulsified oil content of the particular PCP containing waste stream being treated, it may be necessary to apply either of these two processes as pretreatment steps prior to RO and/or GAC polishing in order to protect these polishing steps from oil fouling. The applicability of ultrafiltration will have to be evaluated with bench-scale testing before going to a pilot scale. In the second method, lowering the groundwater pH below 4 will allow a larger fraction of the PCP concentration to be separated with the oil phase. The oil coalescer will then remove emulsified oil and residual free oil in the aqueous phase prior to GAC treatment.

The efficiency of the above two pretreatment methods rely on the presence of significant amounts of fuel grade oil to provide an organic phase in which PCP can be absorbed. In cases where only trace quantities of oil are present, PCP levels up to its maximum solubility (approximately 20 ppm at 30°C) may exist in in the groundwater. In such cases, RO treatment would be recommended prior to GAC polishing to ensure that the design effluent quality can be achieved and to minimize the volume of GAC requiring disposal.

In order to compare the economics of several alternative combinations of treatment processes, ballpark capital and operating costs were developed for three different treatment scenarios. These are presented in Table 5. The costs were estimated for processing 10 pgm of groundwater contaminated with 200 ppm PCP with significant levels of fuel grade oil.

Table 5
Ballpark Capital and Operating Costs

	Scenario 1 Gravity Settling/ Oil Coalescing/ RO/GAC	Scenario 2 pH Adjust/ Gravity Settling/ Oil Coalescing/GAC	Scenario 3 Gravity Settling/ Oil Coalescing/ NF/GAC
Capital Costs			
Settling Tank (2400 gal)	4000	4000	4000
Oil Coalescer	3000	3000	3000
Membrane System	45000	-	45000
GAC System	28000	28000	28000
Acid Metering Pump	-	1000	-
Total Capital Cost	**$80,000**	**$36,000**	**$80,000**
Annual Operating Costs			
Electricity	3000	1000	2000
Membrane Replacement	4000	-	4000
Misc. Supplies/Chemicals	2000	6000	2000
Activated Carbon	7000	35000	13000
Concentrate Disposal	160000	-	32000
Carbon Disposal	1000	5000	2000
Operating Labour	7000	7000	7000
Maintenance	4000	2000	4000
Total Operating Cost	**$188,000**	**$56,000**	**$66,000**

Costs (in Canadian $) are based on testing groundwater flow of 10 gpm.

In Scenario #1, the treatment process involves gravity settling, oil coalescing, RO and GAC polishing. The RO unit contains eight 4" x 40" membranes, a 10 Hp pump and a clean-in-place system for intermittent cleaning of the membranes. The membrane life in this application was estimated to be about two years. The GAC system consists of a pump, two carbon columns in series each capable of hold 15 ft3 of carbon and a backwash tank. The carbon beds should last for a minimum of 4 months and possibly as long as 6 months if the RO permeate quality can be reasonably sustained. Chemical requirements include membrane cleaners and an antiscalant to permit scale-free operation at a 95% recovery level.

Scenario #2 involves pH adjustment, gravity settling, oil coalescing and GAC treatment. An acid metering pump would be required to reduce the pH of the incoming groundwater below 4 with 20% hydrochloric acid. After gravity settling and oil coalescing, the feed to the GAC columns was assumed to contain about 2 ppm PCP and 50 to 100 ppm TOC. These are only rough estimates and some confirmatory bench-scale tests would have to be conducted before applying this pretreatment procedure in the field. The rebedding frequency for the GAC columns were estimated to be once every two weeks in this case.

In Scenario #3, the treatment process consists of gravity settling, oil coalescing, nanofiltration and GAC treatment. Nanofiltration is essentially a hybrid of reverse osmosis and ultrafiltration (UF) since the membranes used are looser than RO membranes but tighter than UF membranes. Nanofiltration would reject at least 50% of the PCP at feed pressures of only 200 psi. Since there is significant passage of dissolved organic and inorganic species through the membrane, the increase in osmotic pressure at high recovery levels would be significantly less than in RO systems thereby permitting the process to be operated at higher recoveries than RO. In this particular economic assessment, nanofiltration was assumed to give a 60% rejection of PCP and an average flux of 14 gfd when operating at a feed pressure of 200 psi and a recovery of 99% (i.e. a twenty-fold concentration of the feed). By operating at a 99% recovery level as opposed to a 95% recovery level in Scenario #1, there was an 80% reduction in concentrate disposal costs giving Scenario #3 much lower operating costs compared to Scenario #1. The nanofiltration system consists of either 4" x 40" membrane modules, a 4 Hp pump and a membrane clean-in-place system. The carbon beds were estimated to last 5 weeks assuming PCP and TOC levels below 1 ppm and 10 respectively in the feed to the carbon columns. Chemical requirements are for membrane cleaners and antiscalant.

Disposal costs were included as an operating cost for each scenario. The rates used are those charged by Canadian waste incineration facilities and do not include haulage costs.

Scenario #2 was found to have lowest operating costs at $56,000 annually. Scenario #2 also required the lowest initial capital investment at #36,200. Scenario #1 had very high operating costs due primarily to the high cost of concentrate disposal by incineration. The results of this economic analysis demonstrate the large effect disposal costs can have on the viability of a treatment process. If either of the RO or NF concentrates could be potentially reused in a wood preserving process, the outcome of this economic analysis would have favored Scenario #1. These options available must therefore be evaluated based on local disposal costs and the potential for concentrate reuse.

It should be emphasized that only the technical feasibility of Scenario #1 has been confirmed with actual testing and that the treatment efficiency of Scenarios #2 and #3 are only assumed at this point. The potential efficacy of all three treatment scenarios needs to be determined and compared before a reliable decision can be made as to the optimal process for treating groundwaters contaminated with PCP and fuel grade oil. The flexibility of the processes for handling groundwaters with varying degrees of contamination will also have to be taken into consideration in future work.

The following conclusions and recommendations have made based on the results of this study:

- PCP rejections of 99% and membrane fluxes of up to 14.2 gfd at a 600 psi feed pressure were obtained in RO tests at a recovery level of 85% and an operating temperature of about 74°F. The results of the study indicate that a full-scale RO system could be operated efficiently at up to 95% recovery (i.e. a twenty-fold concentration of the feed) provided suitable measures are taken to control barium sulphate scaling and remove demulsified oil from the concentrate. Barium sulphate scaling can be controlled by dosing the feed with an antiscalant, while oil removal can be accomplished by gravity separation and oil coalescing.

- GAC polishing of the RO permeate reduced the PCP concentration in 6,350 bed volumes of permeate from 52 ppb to an average of 0.92 ppb giving an operating adsorption capacity of 0.6 mg/ PCP/g carbon.

- An economic assessment of three different treatment scenarios showed pH adjustment/gravity settling/oil coalescing/GAC treatment (Scenario #2) to be the most economically attractive, while gravity settling/oil coalescing/RO/GAC polishing (Scenario #1) had operating costs at least three times greater than Scenario #2 primarily because of the high cost of concentrate disposal by incineration. However, Scenario #1 would be strongly favoured over the other scenarios in cases where the RO concentrate can be reused.

- The technical feasibility of only Scenario #1 was confirmed in this study. ZENON therefore recommends that future treatability testing focus on evaluating the efficiency of all three scenarios to confirm the assumptions made in estimating their capital and operating costs. Testing should be conducted at a pilot-scale to obtain more realistic operating data.

CASE 3 POTENTIAL APPLICATION OF MEMBRANE/ BIOLOGICAL TREATMENT FOR THE REMOVAL OF PENTACHLOROPHENOL FROM GROUNDWATER

Background

During the 1970's a novel wastewater treatment system was developed consisting of a suspended growth biological reactor coupled to a membrane ultrafiltration unit . With improved membrane chemistries and configurations, this process has become cost competitive with conventional biological treatment systems particularly for difficult to treat industrial effluents and contaminated groundwaters. ZENON's patented membrane/biological treatment process (the ZenoGem™ process) was developed in partnership with General Motors (US) to deal with complex water soluble organic compounds which are being used increasingly in the metalworking industry in Canada and the United States.

These complex mixtures of dissolved and emulsified organics are difficult to treat by conventional physical,chemical and/or biological treatment methods. The first full scale ZenoGem™ facility was designed and built at GM's plant in Mansfield Ohio. This plant has operated successfully since its startup in 1991.

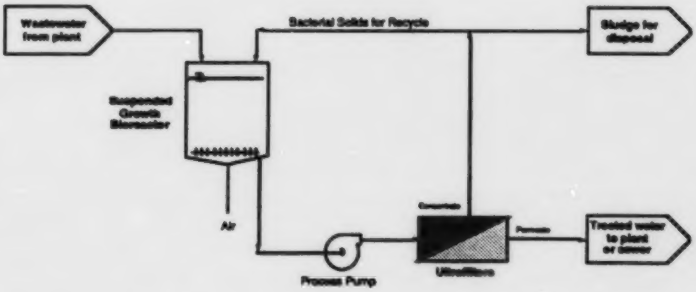
The ZenoGem™ process is now in various stages of development and/or commercial application on a wide range of wastewater streams that are high in concentration, difficult to degrade or, are highly variable in concentration. It is because of the particular benefits of this process compared to conventional physical/chemical and biological treatment processes that this process is expected to be effective on PCP contaminated wastewaters. These benefits are outlined in the following sections.

Process Description

The ZenoGem™ process consists of a biological reactor integrated with an ultrafiltration membrane system (Figure 1). The ultrafilter not only filters the treated water prior to discharge and recycles the biological solids to the bioreactor, but it also recovers the higher molecular weight soluble materials that would otherwise pass through conventional clarifiers and filters. These higher molecular weight materials are returned to the bioreactor for further biodegradation prior to ultimate discharge.

Figure 1

The ZenoGem™ Process Schematic


Wastewater from plant
Bacterial Solids for Recycle
Sludge for disposal
Suspended Growth Bioreactor
Air
Concentrate
Permeate
Treated water to plant or sewer
Process Pump
Ultrafilters

Ultrafiltration (UF) is a pressure-driven cross flow filtration process in which the water to be processed flows tangentially over the surface of a membrane filter capable of separating both insoluble materials (bacteria, colloids, suspended solids) and higher molecular weight soluble materials from the treated water. The filtrate and the retentate are commonly referred to as permeate and concentrate respectively (Figure 2). The threshold size above which organics are retained by the membrane and below which they pass through the membrane is called the molecular weight cut-off. This ranges between 3,000 and 100,000 Daltons (0.003μ to 0.1μ) and is dependent upon the specific membrane chemistry. The ultrafiltration spectrum in comparison with other cross flow filtration processes (reverse osmosis, microfiltration) is presented in Figure 3. In the ZenoGem™ process, the concentrate is recycled to the bioreactor while the permeate is discharged. The typical operating pressure of a UF system is 60 - 70 psi.

Figure 2

Cross Flow Filtration

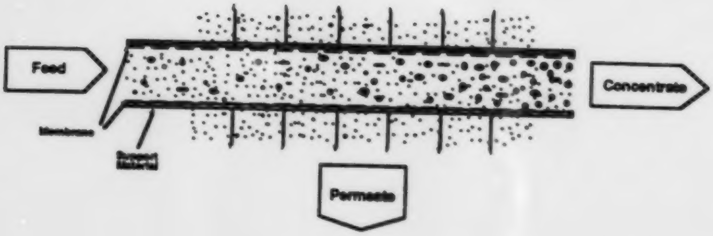
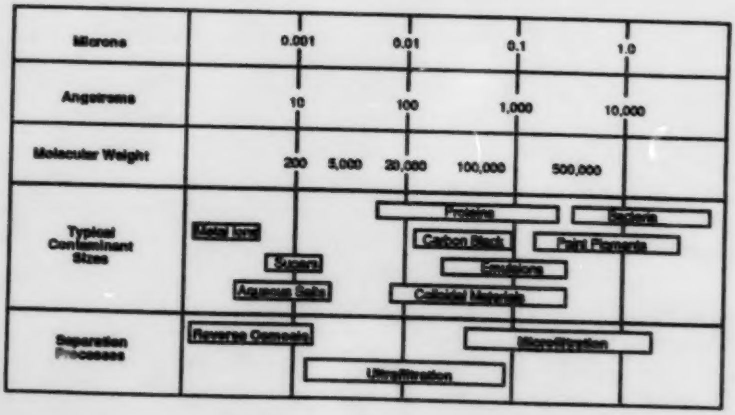


Figure 3

Filtration Spectrum



Benefits

The ZenoGem™ process has significant technical and economic benefits over alternative processes e.g. activated sludge with clarifiers or physical-chemical treatment:

1) Improved Effluent Quality

The ultrafiltration membrane provides a positive means of solid-liquid separation thus preventing the loss of biological solids in the effluent. Certain soluble organics, e.g. emulsified oil and grease, are also retained thereby further improving the effluent quality. In 36 samples collected during a 12 month pilot study at an automotive parts manufacturing facility, the effluent TSS averaged <7 ppm and the effluent hydrocarbon oil & grease averaged <5 ppm.

2) Reduced Sludge Production

In contrast with conventional physical-chemical and biological waste treatment processes, the volume of sludge produced is significantly reduced since chemicals are not required for precipitation/coagulation reactions and high sludge retention times (in the order of 75 - 100 days) are provided in biological systems. Based on the results of the same 12 month study referred to in #1 above, the client estimated that sludge production would be reduced by ~ 90% in comparison with an existing dissolved-air flotation/fluidized bed bioreactor system.

3) System is Less Vulnerable to Upsets

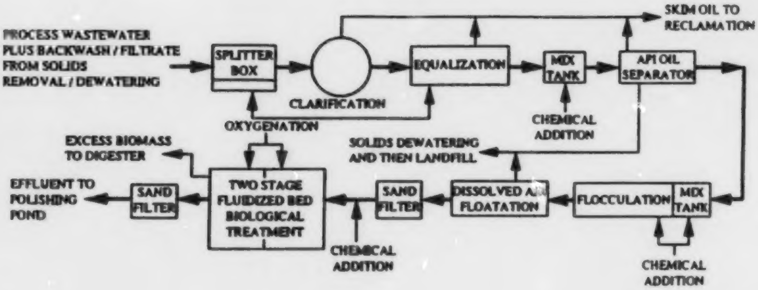
Since the ultrafilter performance is not dependent upon settleability of the biological floc, the biological solids are still retained even if an upset in the bioreactor occurs e.g. due to chemical or pH shock or due to variations in organic loading. This is in contrast with a conventional clarifier where performance depends on the settleability of the floc.

If an upset occurs in a conventional system and a difficult-to-settle "pin floc" or "filamentous floc" forms, the biological solids can easily be lost. In the short term, an effluent high in suspended solids and BOD5 will be produced and in the long term, effluent with high BOD5 will be produced until the biological population is restored.

4) Capability to Handle High Strength, Complex Industrial Wastewaters

Biological wastewater treatment processes are widely used to remove organic compounds. Conventional biological processes however, often fail to degrade industrial wastewaters adequately. These systems frequently fail if wastewaters have a high BOD, or contain many different types of compounds (complex) or exhibit a wide fluctuation in strength. They usually fail through the loss of bacteria over the clarifier weir as mentioned above. In the ZenoGem™ process no such losses occur and as a result all kinds of difficult to treat industrial wastewaters are treated reliably; as such, even oil can be degraded in a ZenoGem™ system.

Figure 4
Simplified Process Schematic of General Motors Industrial Wastewater Treatment Plant


SKIM OIL TO RECLAMATION
PROCESS WASTEWATER PLUS BACKWASH / FILTRATE FROM SOLIDS REMOVAL / DEWATERING
SPLITTER BOX
EQUALIZATION
MIX TANK
API OIL SEPARATOR
CLARIFICATION
OXYGENATION
CHEMICAL ADDITION
EXCESS BIOMASS TO DIGESTER
SOLIDS DEWATERING AND THEN LANDFILL
EFFLUENT TO POLISHING POND
SAND FILTER
TWO STAGE FLUIDIZED BED BIOLOGICAL TREATMENT
SAND FILTER
DISSOLVED AIR FLOATATION
FLOCCULATION
MIX TANK
CHEMICAL ADDITION
CHEMICAL ADDITION

Physical/chemical processes can produce up to 1 kg of sludge for each kg of waste. Conventional biological processes produce typical 0.2 to 0.6 kg of sludge for each kg of BOD. In comparison, ZenoGem™ produces only about 0.1 kg of sludge per kg of BOD.

5) Compact, Modular Unit

The ZenoGem™ system is quite compact. Its space requirement is usually less than 30% of the space required for an equivalent conventional biological system.

Commercial Operation

One example of commercial operation mentioned previously in automotive manufacturing is that of General Motors where several plants have evaluated the

ZenoGem™ process. Application of the ZenoGem™ process to this type of plant, along with various alternatives, are reported by General Motors, with ZenoGem™ being the clear choice (Figure 5) in terms of effluent quality, ease of operation, and operating economics compared to existing conventional technology which is currently in use for this type of complex wastewater. Specific effluent quality for the General Motors study is given in Table 1, indicating that BOD5 <5 mg/L are routinely attained, with corresponding levels of free oil & grease. The feed COD and oil and grease in this case are somewhat higher than that which would be expected for typical PCP contaminated groundwater.

Figure 5

Performance Comparison of ZenoGem™ with Physical/Chemical and Oxytron Treatment

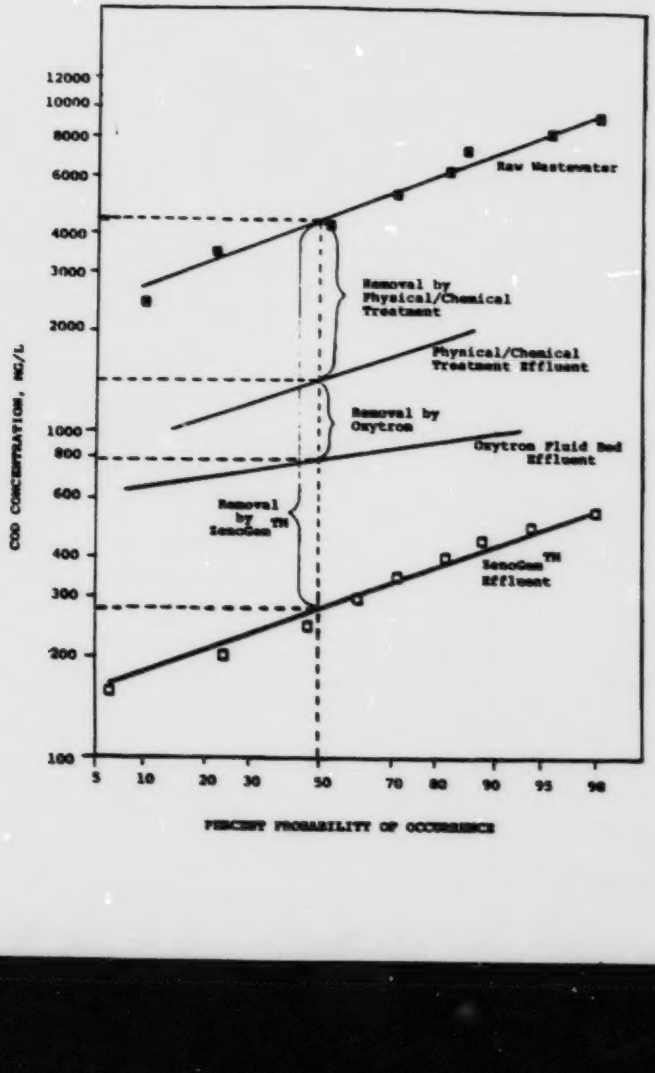


Table 1

ZenoGem™ System Plant Performance During Operation Under Equilibrium Conditions[a]

Analytical Parameters	Sampling Interval P2-1	P2-2	P2-3	P3-1	P3-2
Feed Values, mg/l					
COD	4496	6052	4345	6864	5937
BOD_5[b]	1010	1360	919	1206	1043
TSS	253	817	346	889	410
Total FOG	457	657	714	907	788
Hydrocarbon based FOG	278	352	244	307	403
TKN	68	49	79	43	59
Effluent Values, mg/l					
COD	302	238	183	664	417
BOD_5	4	3	3	34	21
TSS	10	6	11	6	1
Total FOG	17	11	9	36	16
Hydrocarbon based FOG	5	4	3	5	5
NH_3N	0.4	1.3	0.2	4.2	0.8
TKN	0.7	2.1	5.2	7.7	4.7

[a] All values stated are means during operating period. TSS represents total suspended solids and FOG represents fats, oils and grease.

[b] Calculated from COD to BOD_5 correlation based on analysis of all paired analytical data available during treatment of each wastewater.

Summary

The ZenoGem™ process represents a major advancement in treatment of complex and oily wastewaters to dischargeable limits. Because of its ease in retrofit to existing wastewater treatment operations, and its relatively low capital and operating costs, it is making a major impact in industries ranging from metal finishing, to specialty chemicals (detergents, surfactants, other), to food/beverage, as well as contaminated groundwaters and leachates. The particular benefits of this process for difficult to treat wastes make potentially well suited to the treatment of PCP contaminated water. Pilot scale test data are required to verify the performance and costs of the ZenoGem™ process for this particular application.

EFFICACY OF STEAM STRIPPING IN REMOVAL OF DICHLOROMETHANE FROM GROUNDWATER

Laboratory and Pilot Scale Studies

by

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ABSTRACT

The applicability of steam stripping as a remedial technology to remove dichloromethane from contaminated groundwater has been evaluated in laboratory and pilot scale field studies. Laboratory evaluation using contaminated groundwater containing up to 5,200 ppm dichloromethane demonstrated that greater that 99% removal efficiencies could be achieved using a two pass system.

Based on the laboratory evaluation, a six month pilot scale field trial was conducted at a contaminated groundwater site in the Toronto area. Groundwater containing up to 9,700 ppm dichloromethane was fed to Environment Canada's 2,000 L/h mobile steam stripping unit at an average rate of 900 L/h. Under optimum conditions greater than 99.99% removal efficiencies were achieved on a single pass through the unit. Slightly lower removal efficiencies (99%) were obtained under continuous operating conditions.

Greater than 99.99% removal efficiencies have been routinely achieved in the field using a two pass treatment process. Under these operating conditions the treated groundwater contains less than 1ppm dichloromethane.

Relative to other remedial technologies for the treatment of contaminated groundwater, steam stripping has been shown to be an economically viable and environmentally sound alternative for the removal of dichloromethane from groundwater.

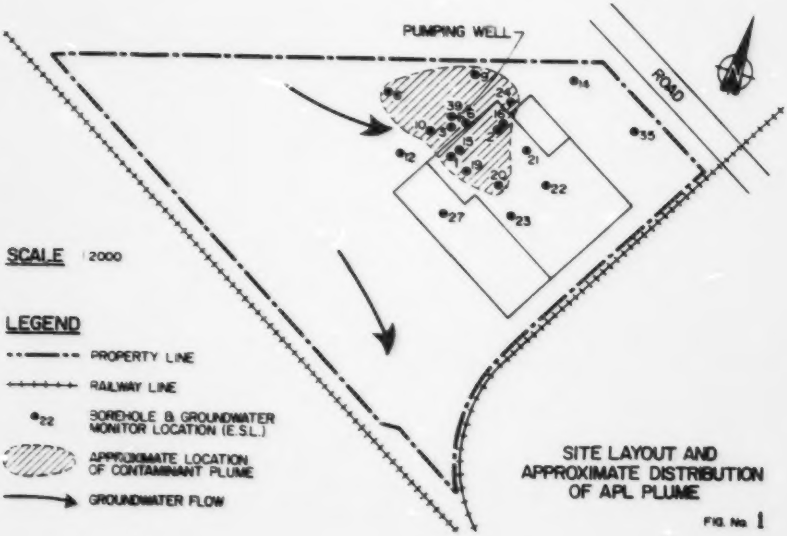
INTRODUCTION

Numerous pump and treat technologies are available to assist in the remediation of groundwater contaminated with organic chemicals. Some of the commercially available systems, however such as air stripping and activated carbon adsorption either merely transfer pollution from one medium to another or are too expensive to be economically viable. The use of steam stripping to remove volatile organic contaminants (VOC's) from groundwater is an alternative approach which is both environmentally safe, since the contaminant being recovered is not discharged to the environment and cost effective in terms of unit operation and contaminant disposal[1].

The following paper describes the results of laboratory and pilot scale field studies to evaluate the suitability of steam stripping as a remedial technology to remove dichloromethane (DCM) from groundwater.

SITE HISTORY AND DESCRIPTION

Marshall Macklin Monaghan Limited were retained by an industrial client to evaluate and implement the most cost effective remedial strategy to decontaminate soil and groundwater at an industrial facility in Toronto, Ontario. Groundwater at the facility had been contaminated with DCM when an underground tank ruptured during filing, in the early 1970's. Following the incident the tank was repaired in-situ and was used for solvent storage until its removal in 1989. During decommissioning of the site it was discovered that the original tank rupture had produced an aqueous phase liquid (APL) contaminant plume and possibly a dense non-aqueous phase liquid (DNAPL) which extended beneath the manufacturing facility and covered an area of approximately 40 m by 60 m (Figure 1).


PUMPING WELL
ROAD
39
6
10
3
15
2
16
24
8
9
1
19
20
12
14
35
21
22
27
23
SCALE 1:2000
LEGEND
PROPERTY LINE
RAILWAY LINE
22
BOREHOLE & GROUNDWATER MONITOR LOCATION (E.S.L.)
APPROXIMATE LOCATION OF CONTAMINANT PLUME
GROUNDWATER FLOW

SITE LAYOUT AND
APPROXIMATE DISTRIBUTION
OF APL PLUME

FIG. No. 1

GEOLOGIC AND HYDROGEOLOGIC SETTING

Ground surface slopes gently towards the southeast corner of the property and has approximately three meters relief.

The site is located near the contact of three Quaternary units: shallow and deep lacustrine sediments and the Wildfield Till. The lacustrine sediments are part of the Lacustrine-Wildfield Till Complex. These deposits consist of both fine-grained silts and clays as well as coarser grained sand and gravel deposits. Interstratified with the coarser sediments can be till-like sediment similar to the Wildfield Till. Underlying the lacustrine Wildfield Till complex is the dark grey, fine grained Wildfield Till. The Halton Till and older interglacial fluvial and alluvial sediments may underlie the Wildfield Till and at depth the Wentworth and Sunnybrook Till may also be present.

The drilling program conducted on the site revealed a complex stratigraphy of interstratified silts and clays as well as coarser sands, gravel and till. The stratigraphy on the site consists of approximately 2 meters of reworked sandy silt of unknown origin, perhaps fill or coarse grained deltaic sediment. Underlying the reworked sediment is approximately 9 meters of the Lacustrine-Wildfield Till complex. This forms a fining upward sequence from interstratified Wildfield Till and gravel at approximately 9.5 meters depth to a silty clay at 2 meters depth. Underlying the Wildfield Till is approximately 4 meters of stratified silts, sands and gravels associated with older alluvial and fluvial deposition. At approximately 14 meters depth an older till unit is found, possibly the Halton Till.

The hydraulic conductivity of the Lacustrine Wildfield Till complex, where most of the groundwater contamination was detected was 3.7×10^{-4} cm/s as measured by falling head piezometer tests. The hydraulic conductivity for the deeper, less contaminated aquifer beneath the Wildfield Till unit was 9.0×10^{-4} cm/s. The direction of groundwater flow in the Lacustrine Wildfield Till complex beneath the plant is towards the south east. Groundwater flow direction in the lower aquifer was not determined.

GROUNDWATER CHEMISTRY

Initial groundwater chemistry data indicated that contamination was largely confined to the upper aquifer located in the Lacustrine Wildfield Till complex. The main contaminant found in this zone was DCM which was detected in concentrations approaching the upper solubility limit of DCM in water (20,000 ppm @ 20°C). Smaller concentrations of other chlorinated aliphatic and unchlorinated aromatic compounds (Table 1) were also detected. The high concentration of DCM detected in groundwater suggested that a plume of DNAPL might be present in the immediate area of the original spill and possibly beneath the manufacturing facility.

Dichloromethane was the predominant contaminant detected in the lower aquifer located beneath the Wildfield Till Unit. The maximum DCM concentration detected in this zone was 160ppm, several orders of magnitude less than detected in the upper aquifer[2]. The two aquifers are thought to be separated by a semi-permeable till layer which forms the bottom of the Wildfield Till complex. Pump tests have shown that the two aquifers are interconnected to some degree although the difference in DCM concentration suggests that the interconnection is not intimate.

Given the time that has elapsed since the occurrence of the DCM spill it is surprising that the areal extent of contamination was not significantly larger. The probable reason for this is that the Wildfield Till unit which appears to have retarded the downward migration of DCM to the lower aquifer, rises by several meters in a south easterly direction beneath the plant building. This elevation of the till unit therefore presents a physical barrier which has contained the DCM spill to the relatively localised area indicated in Figure 1.

REMEDIAL STRATEGY DEVELOPMENT

The remedial options considered to decontaminate soil and groundwater on the site included biodegradation, excavation and removal, in-situ stabilization, in-situ containment and vacuum extraction coupled with pump and treat technology. The lateral and vertical containment of the contaminant plume by the geology of the site together with the fact that a significant portion of the contaminant plume lay beneath the manufacturing facility were major factors in the selection of a remedial option. Vacuum extraction and pump and treat technology were determined to be the most cost effective remedial strategy to decontaminate soil and groundwater on the site. In view of the high cost generally associated with groundwater remediation, a pilot scale study was considered necessary in order to evaluate the feasibility of the pump and treat component of the overall strategy prior to moving to a full scale treatment system.

TABLE 1. MAXIMUM CONTAMINANT CONCENTRATIONS DETECTED IN GROUNDWATER

CONTAMINANT	CONCENTRATION (ppm)
Dichloromethane	25000
1,1-Dichloroethene	4.50
1,1-Dichloroethane	36.80
Chloroform	0.35
1,1,1-Trichloroethane	4.80
Trichloroethene	1.04
Dibromochloromethane	0.01
Tetrachloroethane	3.50
Toluene	26.00
o,m,p-Xylene	1.02

The Emergencies Engineering Division of Environment Canada were known to be actively pursuing the potential of steam stripping as a groundwater remediation technology and had built both a bench scale and a pilot scale unit. Marshall Macklin Monaghan Limited therefore approached the Emergencies Engineering Division for assistance in evaluating the efficiency of steam stripping in removing DCM from groundwater.

The United States Environmental Protection Agencies Risk Reduction Engineering Laboratory's treatability database was accessed to evaluate the known efficiencies of various pump and treat technologies in the removal of DCM from water. The data indicated that of the available technologies, steam stripping gave the greatest removal efficiencies for DCM concentrations greater than 1 ppm. Compared to alternative, more established VOC treatment technologies such as air stripping and activated carbon adsorption, steam stripping was considered to be more cost effective. With air stripping significant costs would be incurred in meeting current air emission standards. Similarly the lower removal efficiency of activated carbon coupled with the regeneration and/or disposal of DCM contaminated carbon waste tended to make it more expensive.

STEAM STRIPPING PROCESS

Steam stripping is a separation process that utilizes differences in the thermodynamic properties of liquids. It is a process by which one or more components of a liquid mixture (usually water and an organic species) is transferred to the vapour phase. The driving force for the separation is the concentration differential of the organic component(s) between the liquid and vapour phases. Removal efficiency is highly dependent on a number of factors including Henry's Law Constant, temperature, vapour pressure and steam-to-water ratio. An increase in any of these parameters produces a corresponding increase in removal efficiency, assuming that all other factors remain constant[3]. Other factors which influence removal efficiencies include size and type of column packing and the ratio of column diameter to packing diameter.

ANALYTICAL METHODS

Dichloromethane concentrations in water were measured by purge and trap gas chromatography during the laboratory and optimization portion of the trials. A photo ionization detector gas chromatograph capable of measuring DCM levels down to 0.1 ppm, was used for analysis during the field scale evaluation.

LABORATORY SCALE EVALUATION

Laboratory scale evaluation showed that DCM could be removed from groundwater using steam stripping[4]. Greater than 99% removal efficiencies were achieved when operating at near optimum conditions. In the laboratory experiments, the feed rate was varied between 70 and 194 mL/min with a run time which varied from 5 to 30 minutes. Steam was fed at a constant rate of 9.2 g/min resulting in a feed-to-steam ratio which varied between 7.5 and 21.

As part of the optimization procedure, contaminated groundwater was fed to both the middle and top of the column. Theoretically, a feed point near the middle of the column and a low feed to steam ratio would enhance DCM removal. Laboratory scale results however, showed only a small increase in removal efficiency when groundwater was fed to the middle of the column. The laboratory scale evaluation indicated that DCM removal efficiencies of greater than 99.9% could be achieved in the pilot scale steam stripping unit using a two pass system. The DCM concentration in groundwater could therefore be reduced from an average value of 3,500 ppm to less than 1 ppm.

High levels of calcium were detected in groundwater during the laboratory evaluation. The high calcium levels were associated with high pH levels in the groundwater samples. In order to minimize scaling in the steam stripping unit, various pre-treatment methodologies to reduce the calcium levels were investigated. Scale build up would reduce the throughput of the unit and could affect DCM removal efficiencies. It was shown that calcium precipitation would not occur if the pH of the groundwater was between 6.5 and 8.5 units. It was decided therefore that if high pH groundwater was encountered during the field trial, sulphuric acid would be added to bring the pH below 8.5.

FIELD SCALE EVALUATION

The process flow diagram for the field scale trial is shown in Figure 2. The pH of the groundwater was monitored during the optimization portion of the trial to determine whether pre-treatment would be required prior to feeding to the steam stripper. The average pH of pumped groundwater was 7 units, therefore pre-treatment was not necessary.

During the seven optimization runs, contaminated groundwater was introduced either at the top or to the middle of the column. Steam was provided by a 1,150,000 kJ/h oil fired burner. Although the design flow rate for the feed was 2,000 L/h, the flowrate obtained during the optimization run varied from 900 L/h to 450 L/h resulting in a corresponding variation in the feed to steam ratio of 2 to 4.5. The length of steam stripping runs varied from 45 minutes to almost five hours. Run length was normally determined by the tank space available to store the treated groundwater. Based on the results of the laboratory evaluation agreement was reached with the local authority to discharge treated groundwater with a DCM concentration of less than 1 ppm to sanitary sewer.

Preliminary results from these tests (Table 2, Runs 1 to 7) showed that when the groundwater was fed to the top of the column, removal efficiencies of up to 99.7% were achieved in a single pass and up to 98.7% removal was achieved in the second pass[5]. The overall removal efficiency therefore for two passes through the unit was up to 99.99% which gave DCM levels of less than 1 ppm in the treated groundwater.

DCM removal rates increased slightly when the groundwater was fed to the middle as opposed to the top of the column. After one pass, the removal percentage varied from 99.7% to 99.99% which gave DCM levels as low as 0.9 ppm in the first pass treated water. A second pass through the unit reduced DCM levels to 0.7 ppm.

Optimal operating conditions for the field trial were therefore realized by feeding to the middle of the column at maximum steam flow.

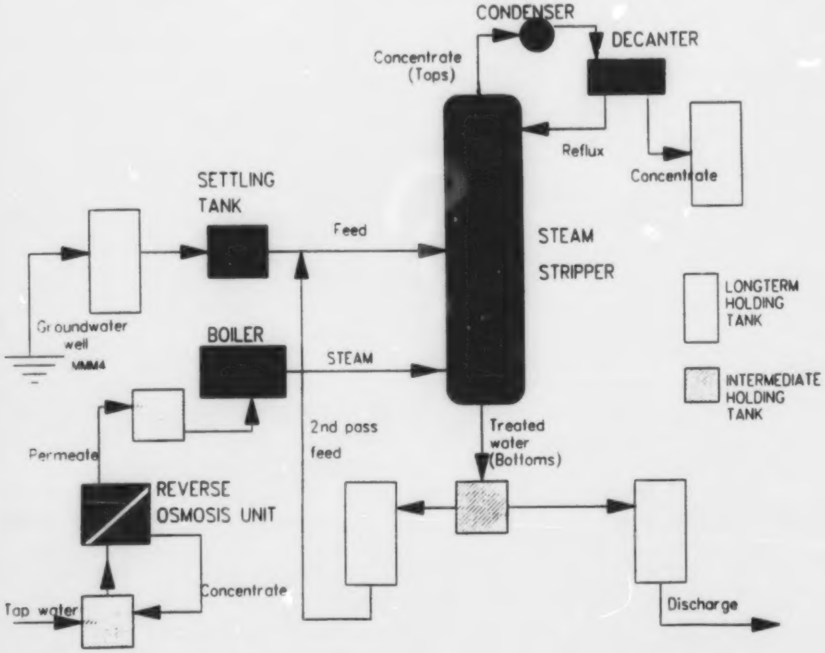

CONDENSER
DECANTER
Concentrate
(Tops)
Reflux
Concentrate
SETTLING
TANK
Feed
STEAM
STRIPPER
LONGTERM
HOLDING
TANK
Groundwater
well
MMM4
BOILER
STEAM
INTERMEDIATE
HOLDING
TANK
Permeate
2nd pass
feed
Treated
water
(Bottoms)
REVERSE
OSMOSIS UNIT
Concentrate
Tap water
Discharge

Figure 2. Field Scale Process Flow Diagram

TABLE 2. CONCENTRATIONS AND PERCENT REMOVALS OF DICHLOROMETHANE

RUN NO.	FEED DESCRIPTION	FEED LOCATION	TIME (min)	CONCENTRATION FEED (ppm)	CONCENTRATION BOTTOMS (ppm)	PERCENT REMOVAL
1	groundwater	top	45	9591	63	99.34
			120		130	98.64
2	groundwater	top	45	7993	25	99.69
3	2nd pass	top	30	73	112	0.00
			70		13	82.19
			130		14	80.82
4	2nd pass	top	85	73	0.98	98.66
			130		10	86.30
5	groundwater	midway	60	12605	34	99.73
			175	2328	1.1	99.95
			295	10470	0.9	99.99
6	2nd pass	midway	80	12	3.4	71.67
			220		0.7	94.17
7	groundwater	midway	80	9736	5.7	99.94
			155		2.1	99.98
			230		11.9	99.88
			285	586	0.9	99.85
12	groundwater	midway	195	1091	0.5	99.95
			435	658	3.9	99.41
19	groundwater	midway	30	2152	0.6	99.97
			160	2341	6.5	99.72
29	groundwater	midway	95	1262	3.8	99.70
			470	807	trace	100.00
33	groundwater	midway	90	1096	2.2	99.80
			305	1127	ND	100.00
			470	672	ND	100.00
34	groundwater	midway	80	1436	0.8	99.94
			265	1658	ND	100.00
36	2nd pass	midway	60	13	0.3	97.69
			180		ND	100.00
			290		ND	100.00
			470	7	ND	100.00
40	groundwater	top	210	2987	ND	100.00
			270	2829	ND	100.00
41	2nd pass	top	55	49	ND	100.00
			170	14	ND	100.00
			330	18	ND	100.00
43	groundwater	top	140	1666	ND	100.00
			260	1409	ND	100.00
			345	2924	ND	100.00
44	2nd pass	top	45	21	ND	100.00
			190	1	ND	100.00
			230	trace		

FIELD EVALUATION RESULTS

Contaminated groundwater was treated using the steam stripper over a four month period to evaluate the feasibility of pump and treat technology to remove DCM from groundwater at the site. During this time, approximately 50,000 L of contaminated groundwater was processed. Approximately 6,500 L of a two phase dichloromethane/water mixture was obtained of which an estimated 120 L is pure DCM. The remaining 43,500 L of treated groundwater, having a concentration of less than 1 ppm, was discharged to sanitary sewer. Data for selected runs showing DCM concentration in the feed and treated water and percent DCM removed are presented in Table 2.

For the first month of operation, the flow meter for the feed stream was faulty and an accurate measure of the flowrate was not available until the second month, by which time the flow had decreased from the 900 L/h flow rate achieved in the optimization runs to 200 L/h. The feed to steam ratio therefore was reduced from more than 2:1 to 1:1. Operation of the unit under these conditions is inefficient since large volumes of condensate were produced giving lower DCM concentrations in the condensate. However, by refluxing the condensate, the volume of waste was kept to a minimum. The decrease in the flowrate may be attributed to fouling of the column by suspended solids in the groundwater. The flowrate improved to approximately 900 L/h after rinsing the column with hydrochloric acid (pH 4) and redirecting the feed to the top of the column. Although the optimization study indicated that feed to the middle of the column was preferable, percentage removals were found to be marginally better when groundwater was fed to the top of the column.

At the lower feed rates, removal efficiencies of greater than 99.9% were routinely achieved and in some instances (Runs 29, 33, 34, 40 and 43) the concentration of DCM in treated groundwater after one pass through the steam stripper was below 1 ppm. However, because the performance of the unit was not sufficiently consistent, a second pass was generally required to reduce the concentration of DCM in the treated groundwater to less than 1ppm.

The field trial has demonstrated that steam stripping offers considerable potential as a treatment technology to remove VOC's from groundwater. The long term use of the pilot scale unit has shown that regular rinsing of the column with acidic solution is necessary in order to maintain an optimum feed rate and removal efficiency.

EFFECTIVENESS OF PUMP AND TREAT SYSTEM ON DCM REMOVAL

Prior to commencing the field trial, a 10 cm diameter pumping well with a 1.5 m long screen was installed in the upper aquifer in the area of the original DCM spill. A 5 cm diameter electric pump was installed in the well just above the top of the screen. Groundwater was pumped to the steam stripper feed tank at an average rate of 330 L/h.

The impact of the pilot scale field trial on DCM concentrations in groundwater was evaluated by monitoring groundwater from selected boreholes both within the sphere of influence of the APL plume and on the periphery of the plume. Groundwater in the lower aquifer was also monitored to assess the effect of pumping on the vertical movement of DCM between the two aquifers.

The change in concentration of DCM in the monitoring wells over time are shown in Table 3. The effect of pumping on DCM concentrations in three of the most contaminated wells is illustrated in Figure 3. As expected, quite dramatic reductions in DCM concentrations were achieved initially as highly contaminated groundwater was removed and replaced by previously uncontaminated groundwater. Following this first rush the concentration of DCM in groundwater stabilized at around 400-600 ppm in wells 1 and 24 and around 3500 ppm in well 2C. The DCM concentration in well 2A which was installed in the lower aquifer showed little change over the duration of the trial. It is probable therefore that downward migration of contaminants would not be a potential problem in remediation of this site.

Figure 3. DCM Concentration in Three Monitoring Wells

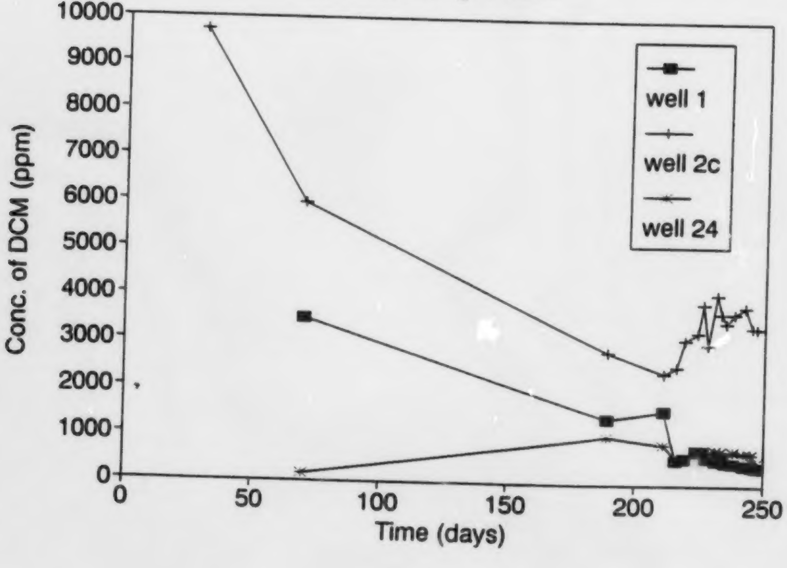


TABLE 3. CONCENTRATION OF DICHLOROMETHANE IN MONITORING WELLS (ppm)

DATE	1	2A	2C	6	8	9	10	12	14	15	21	22	23	24	27	35	39
91 06 03				1400													20.3
91 07 03			9710														
91 08 12	3500	160	5975		0.011	0.007	1.3	0.013	0.009	16800	0.004	0.01	0.008	150	0.003	0.004	
91 12 09	1392		2831		--		--	ND	--		ND	ND	ND	1008	ND	ND	
91 12 31	1571		2384		--		--	ND	--		ND	ND	ND	851	ND	ND	
92 01 05	529		2529		ND		--	ND	ND		ND	ND	ND	591	ND	ND	
92 01 08	568		3102								ND						
92 01 13	732		3277		ND		--	ND	ND		ND	ND	ND	752	ND	ND	
92 01 15	731		3899								ND						
92 01 17	584		3005		ND		--	--	--		ND	ND	ND	695	ND	ND	
92 01 20	538		4089		ND		40							758			
92 01 21		85															
92 01 22	600		3693		ND		--	ND	ND		ND	ND	ND	740	ND	ND	
92 01 24	493		3499		ND									595			
92 01 27	472		3699		ND		18	ND	ND		ND	ND	ND	728	ND	ND	
92 01 31	427		3832		ND		8							678			
92 02 03	411		3389		ND		--	ND	ND		ND	ND	ND	671	ND	ND	
92 02 05	392	161	3372		ND		trace							494			

In order to assess the overall effectiveness of the pump and treat strategy, groundwater pumping was curtailed for a period of one month towards the end of the trial and the change in DCM concentration in each of the wells was monitored. As Figure 3 shows, DCM concentrations remained relatively static in well 1 and 24 and increased only slightly in well 2C before levelling off at around 3400 ppm.

CONCLUSIONS

Based on these preliminary findings, it would appear that a pump and treat system would be a suitable remedial strategy to decontaminate groundwater at this site.

Steam stripping has been shown to be a technically feasible and effective method for removing DCM from groundwater.

The evaluation of the steam stripper indicated that there is not a significant difference in the removal efficiency between feeding to the middle or to the top of the column. Greater than 99.9% of the dichloromethane was removed after two passes through the steam stripper, giving a final discharge concentration less than 1 ppm.

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COMPARISON OF FIRST & SECOND GENERATION ENHANCED PHOTO-OXIDATION FOR THE DESTRUCTION OF WATER BORN ORGANIC CONTAMINANTS

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INTRODUCTION

This paper will compare the first and second generation of ultra violet enhanced oxidation processes (EOP's). The comparison will be made in the areas of:

- UV light sources, spectrum and intensity.
- The chemistry of single and dual path destruction.
- The effect of metal ions in the water on performance.
- The effects of destruction accelerators.

In addition a cost comparison of the second generation EOP and other technologies will be made.

Over the past few years, the use of EOP to treat groundwater contaminated by spills of organic compounds has become more widely accepted by both the regulatory community and those seeking a cost effective solution to their remediation requirements.

EOP is a destruction technology, as such has no secondary disposals/liability issues surrounding its use. The more traditional treatment options such as air stripping or carbon adsorption have this problem. All of these essentially transfer contaminants from one medium to another. In some cases of biological treatment the sludge can be a secondary liability.

EOP technology evolved from a first generation, developed in the 1970's to a second generation developed in the 1980's. As in a lot of promising technologies, the first manifestations are pushed beyond their capabilities. This can give rise to a second generation technology. These are developed to overcome the problems encountered by the first generation when it is pushed beyond its capabilities. This holds true with EOP.

The first generation EOP relied almost exclusively on hydroxyl radical driven destruction. This resulted in the inability to destroy certain compounds.

Also, it suffered from a problem of lamp fouling in numerous applications. The now well proven second generation EOP, ie, RAYOX® (1) technology has significantly improved the application versatility. Also the economics, and performance capability of this inherently attractive treatment alternative has been improved.

FIRST GENERATION EOP

The first generation units use either low pressure or high pressure mercury vapour lamps. These lamps have a very narrow spectrum of UV light, primarily 254 nm (see Figure 1). This narrow spectrum caused the first generation EOP to rely on hydroxyl radicals ($OH^{\bullet}$) for destruction.

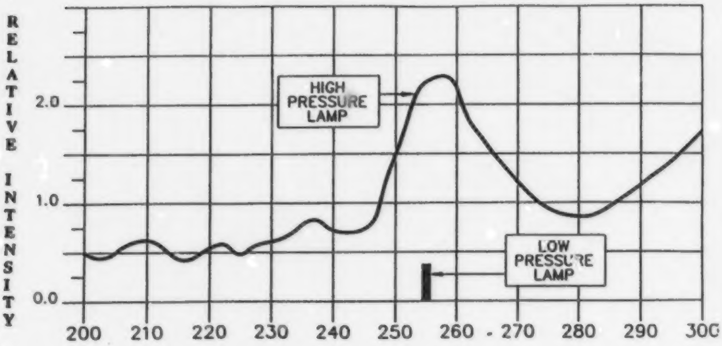
The most common methods of generating the $OH^{\bullet}$ from ozone and/or hydrogen peroxide by exposing them to ultra-violet light are summarized by the following simplified equations:

$$H_2O_2 + \xrightarrow{UV} 2\,OH^{\bullet}$$

$$2\,O_3 + 2\,H_2O_2 \xrightarrow{UV} 2\,OH^{\bullet} + 3\,O_2$$

$$Fe_2 + H_2O_2 \xrightarrow{UV} OH^{\bullet} + Fe_3 + OH^{\bullet}$$

FIRST GENERATION LIGHT SOURCE SPECTRUM AND POWER EMISSION SPECTRA



WAVELENGTH, nm
Figure 1

All of this has been described by several authors (Hoigne and Bader, 1976; Pringle, 1976; Peyton and Glaze, 1988; Paillard, 1988; Skuratover, 1976).

The OH° is 10^6 to 10^9 more reactive than molecular ozone or H_2O_2 (Hoinge and Bader, 1976, 1983). By relying on only the OH° attack, the first generation EOP is limited to a relatively select group of compounds with a high OH° rate content ($\approx 10^8$ litres mol^{-1} sec^{-1}). This includes compounds such as benzene, perchloroethylene, phenol and several PAH's, etc.

However, this limits the range of application for the first generation systems to fast reacting compounds. Nonetheless a reasonably strong base of these applications had been established.

The first generation chemistry can be summarized by the following simplified equation:

$$\begin{array}{c} RH + H_2O_2 \xrightarrow{UV} RH + 2\,OH^{\circ} \\ \downarrow \\ \text{Cascade of Reactions} \\ \downarrow \\ H_2O + CO_2 + (HCl)^{(1)} \end{array}$$

(1) HCl is formed if chlorinated hydrocarbons are present.

The cascades reaction can take from seconds to hours or longer to complete.

Compromising this general success story is:

1) The inability of first generation systems to address successfully compounds who rate constants are less than 10^9 range, ie. chlorinated aromatics, saturated chlorinated compounds, ketones, etc.

2) The hydroxyl radicals indiscriminately attacks all organics present in a given water. This generally gives difficulty in economically treating target organics, coincidentally present in a high concentration of other non-target organics.

3) The presence of dissolved metals such as iron and manganese commonly found in groundwater. This caused fouling or coating of the UV lamps during operation. This phenomenon has generally required additional investment by systems purchasers for appropriate pre-treatment equipment.

Clearly, improvements in the state of the art were needed in order to enhance the efficiency of destruction of a broader range of target compounds. At the same time overcoming some of the chemical and mechanical limitations presented in the first generation.

SECOND GENERATION EOP GENERAL INFORMATION

The implementation of four major design and operational improvements has permitted the second generation as demonstrated in the RAYOX®(2) unit to overcome the inherent limitations in the first generation. These are:

1) An improved UV light source that is more intense and has a broader spectrum of UV-C light.

2) The development of proprietary rate enhancing and selectivity chemical accelerators.

3) An annular, multi-reactor design concept which allows mor flexibility in treatment strategy.

4) Incorporation of an automated lamp wiping mechanism eliminates tube fouling.

SECOND GENERATION LIGHT SOURCE

The RAYOX® proprietary ultra-violet lamp significantly enhances the UV output in the 200-300 nm region especially below 250 nm wave length (2-300 times). This is the range of the UV spectrum where most priority pollutants are photo-chemically most active.

Figure 2 shows the wave length absorptions spectra for several compounds discussed later in this paper. The importance of the obvious skew to the left of the graph becomes evident when one realizes that the increased availability of photons opens a second track of destruction called photolysis. This allows effective treatment of a broader range of compounds including those that do not respond as well to hydroxyl radical attacks. Photolysis involves the interaction of light with molecules to bring about their disassociation into fragments.

Light is composed of tiny energy packets called photons, whose energy (E) is inversely proportional to the wave length of the light:

ABSORPTION SPECTRUM

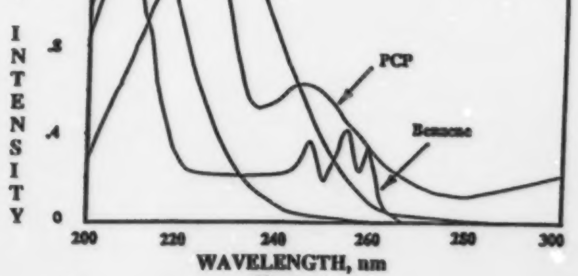


Figure 2

$$E = \frac{hc}{\lambda}$$

Where h is planck's constant, λ is the wave length and c is the speed of light.

Figure 3 shows the comparison of the first generation lamp sources in relationship to the second generation. It should be noted that the RAYOX® has high intensity in the area below 250 nm where as the first generation light sources were very weak in that range.

If absorbtion of photon by a molecule is the cause of photolysis then the photon energy must exceed the energy of the bond to be broken. This requires the wave length to be in the ultra-violet range of the spectrum for most photolysis reactions of organic compounds.

SECOND GENERATION CHEMISTRY

It can be seen that the RAYOX® ultra-violet lamps have 2-300 times more output per watt in this critical UV portion of the spectrum compared to first generation lamps (see Figure 3). Photolysis gives another pathway of destruction in addition to destruction by the hydroxyl radical.

When this is combined with the greater than 90% efficiency of the RAYOX® power supplies driving the lamps, the result is lower operating costs. By the same photolysis mechanism, the generation of hydroxyl radicals from hydrogen peroxide is similarly enhanced. This powerful complementary destruction and rate enhancement mechanism is uniquely available in the second generation systems. A simplified chemistry equation for the second generation is:

$$RH + H_2O_2 \rightarrow 2OH^{\bullet} + RH_1^{\circ} + RH_2^{\bullet} + RH_n^{\circ}$$

$$\downarrow$$

$$\text{Cascade of Reactions}$$

$$\downarrow$$

$$H_2O + CO_2 + (HCl)^{(1)}$$

(1) HCl is formed if chlorinated hydrocarbons are present.

The cascade of reactions in this dual path destruction takes place in Nano seconds to seconds.

SECOND GENERATION ACCELERATORS

Several patented proprietary ENOX® additives or catalytic accelerators have also been identified which can dramatically reduce the UV light input required to destroy the target compound. This is

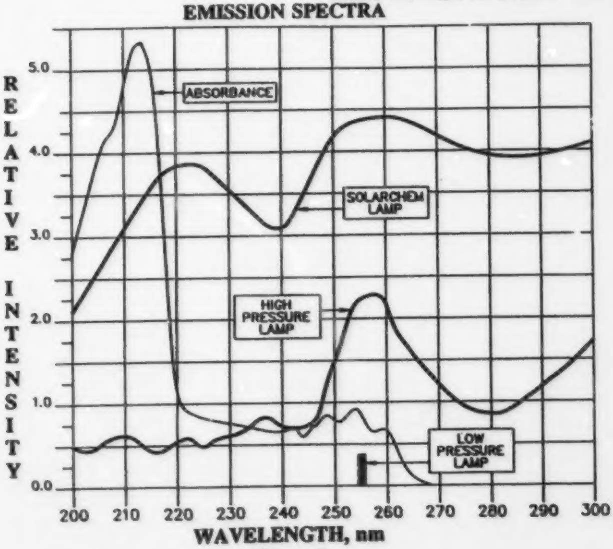


Figure 3

accomplished by the enhancement of the rate of radical formation and the efficiency of their use. This means the second generation systems are sized by the amount of light required per order of magnitude of contaminant reduction per quantity of water treated. Where as the first generation systems are sized by residents time. These additives which are consumed during the RAYOX® treatment can effect a significant capital cost savings often in the range of 20 - 30%. The use of such additives is highlighted in the examples of the examples section of this paper.

Figure 4 makes a comparison of using the following destructions regimens:

1) Ultra-violet light only.

2) Ultra-violet light and hydrogen peroxide.

3) Ultra-violet light, hydrogen peroxide, and ENOX® 510 accelerator.

The vertical axis on Figure 4 is a log scale showing the rate of destruction in parts per billion of benzene. The horizontal scale is an arbitrary RAYOX® dosage number. In this particular graph, it relates to the amount of UV light per thousand gallons required to accomplish destruction. The graph can be analyzed by looking at the vertical axis at the dosage rate of two (2):

1) The top destruction curve shows the rate of destruction using only UV. At a dosage of two (2) it can be seen that the Benzene would be dropped from 8,000 ppb to 7,500 ppb.

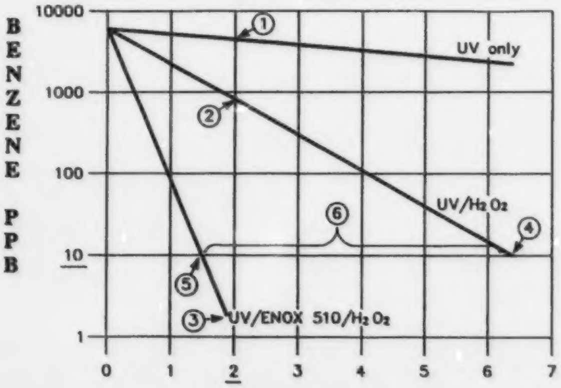
2) The next destruction curve on the graph shows the destruction using UV and H_2O_2. At a dosage rate of two (2) the benzene would be reduced from 8,000 ppb to 900 ppb.

3) The bottom two (2) destruction curves show the use of UV light, H_2O_2, and ENOX® 510 accelerators. The same dosage rate of two (2) will reduce the material from 8,000 ppbs down to 2 ppbs in the case of ENOX® 510.

4) In the case of reducing the effluent to ten (10) ppbs, using only a UV and H_2O_2 it would require 6.5 doseages.

5) However it would require only 1.5 doseages if ENOX® 510 was used.

DESTRUCTION OF BENZENE IN BTEX MIXTURE



RAYOX® DOSE
Figure 4

6) This is a factor of 4 reduction of UV light required. Since 50% of the operating costs is electricity, there would be a significant savings in operating costs by the use of the ENOX® accelerators. In addition, it would reduce the capital costs.

VERTICAL REACTOR DESIGN

The use of the new lamp and accelerators greatly speed up the destruction of target compounds. The reduced time for UV exposure allowed for annular vertical reactor design.

The major benefit of the annular vertical reactor design is its flexibility in optimizing treatment strategy thereby minimizing operating costs (see Figure 5). Because each reactor is a separate entity, treatment can be altered or staged in each reactor. Size, lamp type, and additives can each be varied depending on water characteristics. Chemical usage reductions of up to 30% have been experienced as a result of this unique second generation reactor configuration.

SECOND GENERATION TUBE CLEANER

The compact vertical reactor configuration also makes it easy to incorporate the fourth improvement in the state of the art. This is a patented automated UV lamp cleaning system. The high intensity broad spectrum lamp significantly reduces the number of lamps required. This plus the Vertical Reactor Design allows for a tube wiper. The obvious user benefits are significant reduction in maintenance and system downtime, as well as the ability of the RAYOX® system to handle groundwater containing normal levels of soluble metals, oils, and greases.

WHERE SECOND GENERATION OXIDATION CAN HELP

The following are some general areas where second generation EOP works very well:

1) As the treatment of choice for aqueous organics which are unsuitable for Granulated Activated Carbon (GAC), ie. they are soluble and polar and have a low refractive index or a low Freudlich value <12 (MACL, acetone, VCM, MTBE. NDMA. etc.).

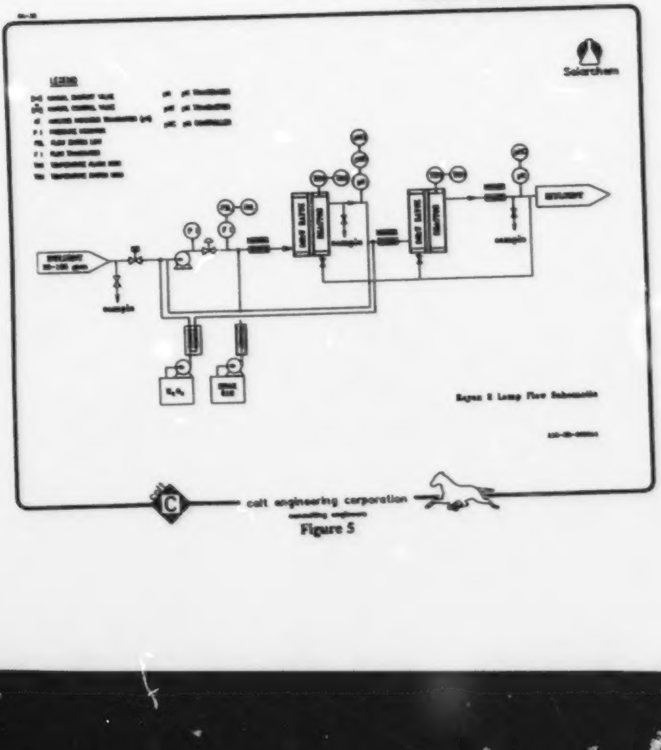


Figure 5

2) As a pre-treatment method to reduce GAC consumption. Avoiding regeneration or destruction costs of GAC.

3) Where the transportation of secondary hazardous compounds such as GAC or membranes is undesirable.

4) As a polishing system for a bio-remediation process where a toxic constituant is vesry slow in biodegradation to greatly increase the capacity of the bio-remediation process.

WATER BORN CONTAMINANTS DESTROYED BY SECOND GENERATION EOP

The following are types and conditions in which RAYOX® second generation units have proven to be effective.

1) Type of compounds.

- Chlorinated methane, ethane and ethylenes.
- Phenols and BTEXs.
- Esters, Ketones, Alcohols, and Solvents
- Pesticides
- Cyanides (free and bonded)
- Nitrogenated compounds
- PCBs, PAHs, VCM, Pherans, Dioxins, etc.
- Vertially any organic

2) In streams which are typically loaded with less than 2,000 ppm of contaminants.

3) Where 3 - 5 orders of magnitude of contamination reduction is desired.

4) Low concentrations of metals < 50 ppm).

5) Where it is desired to run intermittently without start-up problems.

6) Where several different kinds of contaminants streams have to be treated and/or portability is essential.

7) Where continuous operation is required and a minimum of operator time is available.

EXAMPLES OF SECOND GENERATION EOP

To exemplify the diverse applications, as well as the application of its second generation features in specific situations, three examples have been selected as follows:

1) BTEX/MTBE contaminated service station groundwater from LUST.

2) Catalytic treatment of process water containing BTEX/MTBE along with competing non-target organics.

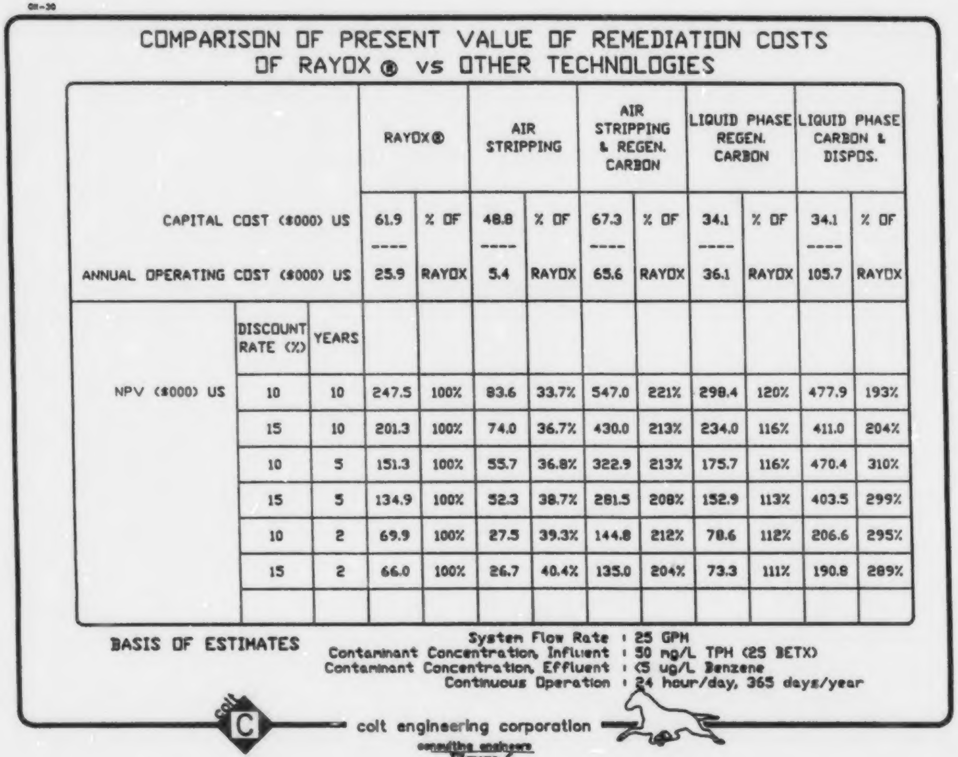
3) Destruction of TPH in water.

LUST BTEX/MTBE/High Fe

Prompted by a desire to reduce the cost of remediating BTEX contaminated groundwater underlying service station sites, a major US oil company has turned to RAYOX®. This replaced Granulated Activated Carbon (GAC) and air stripping. Because GAC cannot effectively remove MTBE, and spent carbon disposal costs are rising dramatically, effective treatment of BTEX and MTBE is accomplished by RAYOX®. No secondary disposal requirements, makes good economic sense. Systems treating 2.5 to 15 GPM have been installed to treat BTEX/MTBE loadings from 15 ppm/5 ppm to less than 5 ppb/10 ppb respectively. In one application, the presence of high metal ion concentrations in the water, which can create operational problems for both GAC and air stripping units, presents no problem to the second generation RAYOX® system with its automated lamp cleaning feature. No iron pre-treatment is necessary.

BTEX/MTBE

A major oil company considered using activated carbon to treat BTEX contaminated water generated by barge ballast, site run-off and tank bottoms at one of its large light product distribution terminals. Treatment costs at one fifth



COMPARISON OF PRESENT VALUE OF REMEDIATION COSTS OF RAYOX ® vs OTHER TECHNOLOGIES

			RAYOX®		AIR STRIPPING		AIR STRIPPING & REGEN. CARBON		LIQUID PHASE REGEN. CARBON		LIQUID PHASE CARBON & DISPOS.	
CAPITAL COST ($000) US			61.9	% OF	48.8	% OF	67.3	% OF	34.1	% OF	34.1	% OF
			----		----		----		----		----	
ANNUAL OPERATING COST ($000) US			25.9	RAYOX	5.4	RAYOX	65.6	RAYOX	36.1	RAYOX	105.7	RAYOX
	DISCOUNT RATE (%)	YEARS										
NPV ($000) US	10	10	247.5	100%	83.6	33.7%	547.0	221%	298.4	120%	477.9	193%
	15	10	201.3	100%	74.0	36.7%	430.0	213%	234.0	116%	411.0	204%
	10	5	151.3	100%	55.7	36.8%	322.9	213%	175.7	116%	470.4	310%
	15	5	134.9	100%	52.3	38.7%	281.5	208%	152.9	113%	403.5	299%
	10	2	69.9	100%	27.5	39.3%	144.8	212%	78.6	112%	206.6	295%
	15	2	66.0	100%	26.7	40.4%	135.0	204%	73.3	111%	190.8	289%

BASIS OF ESTIMATES

System Flow Rate : 25 GPM
Contaminant Concentration, Influent : 50 mg/L TPH (25 BETX)
Contaminant Concentration, Effluent : <5 ug/L Benzene
Continuous Operation : 24 hour/day, 365 days/year

colt engineering corporation
consulting engineers

Figure 6

those of GAC, combined with the coincident ability to easily treat MTBE to low ppb levels, prompted a clear decision in favour of RAYOX®. Second generation system features which make this treatment possible when first generation failed, include the good UV absorption characteristics of BTEX at low wavelengths as well as the staged and catalyzed UV/H_2O_2 addition sequence in the modular RAYOX® design. As in the PCP example cited before, it should be noted that the staged catalyzed treatment regimen allowed selected treatment of the BTEX/MTBE despite the presence of other non-target organics which tended to unduly load the carbon making it a much more costly treatment alternative. Figure 9 shows the destruction curves for a 3 x 30 kW reactor system which treats up to 350 ppm BTEX/MTBE to <10 ppb of each compound at 150 GPM.

While yet other examples of the versatility, and the benefits, of second generation EOP treatment with RAYOX® could be cited, from the largest system in the world treating explosive compounds for the military, to the highly successful treatment of herbicide/ pesticide containing wastewaters for the Environmental Response Team of the US EPA, it is clear that second generation EOP systems like RAYOX® can offer significant cost and performance advantages over earlier EOP systems.

COST COMPARISON OF SECOND GENERATION

A cost comparison of a second generation system has been made with:

- Air stripping only.
- Air stripping with GAC regeneration.
- Liquid phase GAC with GAC regeneration.
- Liquid phase GAC with GAC disposal as a hazardous waste.

The following is a typical contaminated groundwater stream used for a comparison:

- Flow rate: 25 gpm
- Contaminant concentration, influent: 50 mg/L TPH (25 mg/L BETX)
- Contaminant, effluent: <5 mg/L benzene
- Continuous operation: 24 hrs/day, 365 days/year

The net present value of both capital and operating cost of all systems were calculated using discounted cash flow rates of:

- 10%
- 15%

The net present value of each system at each discount rate was calculated for project lives of:

- 2 years
- 5 years
- 10 years

These calculations have been compiled in Figure 6, "Comparison of Present Value of Remediation Cost of RAYOX® vs. Other Technologies". This compilation shows:

- If the lack of regulations allows air stripping only (transfer polutant from water to air only) then the cost is approximately ⅓ of a RAYOX® unit.

- If regulations require that the gas phase of air stripping to be treated, then the RAYOX® system approximately ½ the cost of air stripping with regenerative GAC.

- If a liquid phase system is installed at an operating process plant site and the products from liquid phase GAC regeneration can be put back into the process, then RAYOX® is 20% more cost effective.

- If a liquid phase system is installed on a site where GAC has to be disposed as a hazardous waste or shipped offsite for regeneration, then RAYOX® is ⅓ to ½ the cost.

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(1) A technology developed by Solarchem of Richmond Hill, Ontario.

REAGENT MEMBRANE SEPARATION AS A METHOD OF METALS REMOVAL FROM WATER: THE CASE OF COMPETITIVE BINDING

[EXPANDED ABSTRACT]

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The method of separating and concentrating metal ions, which included selective binding of target ions by water soluble polymers and subsequent ultrafiltration of formed macromolecular compounds from unbound components, has been investigated since the late 60's. During this period, different applications of this method, varying from the removal of toxic components of industrial wastes to the chemical analysis, were developed. It was revealed that almost any metal from the Periodic Table could be separated from other components of a solution using this process [1]. It was shown that microfiltration membranes can be employed instead of ultrafilters [2].

Real groundwater is a multicomponent system where many constituents can interact with a binding agent so that the binding process has a competitive character. This aspect of the separation method was not studied. The main task of the present work was to study the influence of the competing components on the removal of targeted metal ions. The method for selection of polymeric binding agents was elaborated as well.

All tests were performed on real and spiked samples of groundwater. Commercially available water soluble polymers were used as binding agents. Both polymeric and inorganic membranes were employed. Metal and polymer concentrations were analyzed by atomic absorption and UV spectroscopy. The parameter characterizing the effectiveness of membrane separation is the rejection (R) of metals (or a certain metal) by the membrane:

$$R = 1 - C_p/C_f$$

where C_p and C_f are concentrations of the metal(s) in the permeate and in the feed (initial solution), respectively.

It was found that in the case of polymer binding in a multicomponent system, rejection of a metal depends on its affinity towards a polymer. Figure 1 presents the results of the removal of copper, nickel and lead from the spiked solution of a groundwater sample using polyethylenimine as a binding agent. One can see that the selectivity of the rejection at a pH below 6 changes in the order: $Pb^{2+} < Ni^{2+} < Cu^{2+}$, i.e. the higher the affinity of an ion, the higher its rejection by a membrane. It should be stressed that the same correlation exists in the separation of copper - nickel - lead system by weakly basic ion exchange resins.

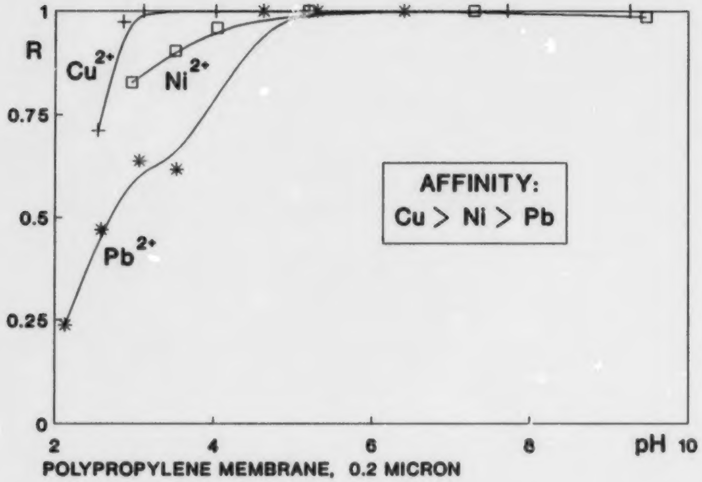

Figure 1. Metals rejection (R) as a function of pH. Polymer: polyethylenimine; metals concentration: 10 ppm; polymer concentration: 100 ppm; transmembrane pressure: 5 psi.

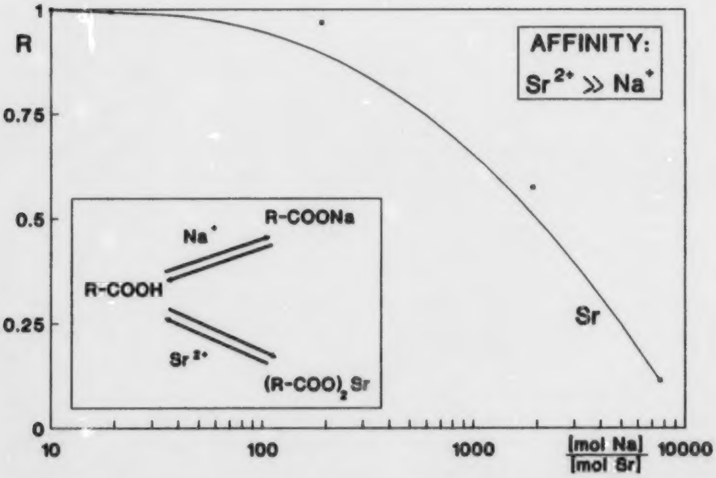

Figure 2. Removal of strontium in the presence of sodium: Rejection (R) vs. the molar ratio of sodium to strontium. Polymer: polyacrylic acid; transmembrane pressure: 5 psi.

The ion of lower a affinity can substantially affect the rejection of an ion of a higher affinity if the former is present at a much higher concentration. The removal of strontium from groundwater in the presence of a large excess of sodium is an example (Figure 2). Even though strontium has much stronger affinity towards polyacrylic acid, the rejection of Sr by a membrane decreases at molar ratios of sodium to strontium 100 and greater. The possible competition in binding must always be taken into account, especially when target components are present in microconcentrations or when the total salinity of a groundwater is high.

A method for the selection of a proper binding agent was suggested. In the case when there is no data available on the binding of an ion in a particular solution by a water soluble polymer, one should find the information on the binding of this ion either by ion exchange / chelating resins or by low molecular agents. Using the analogy between water soluble polymers, on the one hand, and resins or low molecular agents, on the other hand, the desirable structure of a water soluble polymer could be figured out. If such a polymer already exists and is commercially available, it can be tested for the following parameters:

- selectivity towards target components,
- chemical and mechanical stability,
- possibility of regeneration,
- molecular weight,
- toxicity, etc.

If the necessary polymer is not available, it may be synthesized and the product should be tested for the parameters listed above.

Acknowledgement

The authors express their thanks to Dr. Joe Dlouhy of the Chemistry Division, River Road Environmental Technology Centre, for his valuable comments to this work.

Literature

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The Enhanced Oxidation of Pentachlorophenol

by

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ABSTRACT:

This project is concerned primarily with the determination of the effectiveness of enhanced photo-oxidation on a low concentration solution of pentachlorophenol (PCP). The effectiveness of the process will be considered in terms of the time required for the conversion of PCP in the water, to less harmful by-products.

An investigation into the formation of more harmful by-products including polychlorinated-dibenzo-p-dioxins (PCDD's), and polychlorinated-dibenzofurans (PCDF) will be conducted. This will determine the optimum conditions, pH and residence time, for the destruction of PCP at which the formation of PCDD's and PCDF's are minimized.

Since the trials will be performed in the presence of an excess amount of oxidant, a determination of the rate constants for the conversion of the PCP, PCDD's and PCDF's, in terms of the total toxic equivalency (TTEQ), into products will be possible where simple first order kinetics are apparent.

BACKGROUND:

The Emergency Engineering Division of Environment Canada at the River Road Environmental Technology Centre has in the past performed bench scale studies of the enhanced oxidation of waste water contaminated with low levels of PCP. The results of these tests qualitatively determined that the stable, harmful by-products PCDD, and PCDF were formed in the parts per trillion range.

As this is environmentally undesirable, it was essential that the present tests be performed so as to determine the best conditions for the degradation of PCP in water that limited or eliminated the formation of the PCDD's and PCDF's.

In these present tests, as before, the Rayox Reactor (see fig. 1 in Appdx.) technology developed by Solarchem of Richmond Hill, is used. The reactor makes use of a batch type treatment method where the sample being treated is continuously recirculated through the reactor chamber.

In the reaction chamber the sample solution is exposed to the discharge of a 1 KW, high pressure, mercury arc lamp and oxidant. The oxidant used in these experiments is hydrogen peroxide (H_2O_2). When the peroxide molecules are irradiated by the discharge lamp they cleave along the inter-oxygen bond to form the excited state hydroxyl radicals. This species is highly reactive and when in contact with other organic compounds, reacts with them to eventually form carbon dioxide and water.

In the process other simple organics are formed including keytones, aldehydes, alcohols, carboxylic acids, in the case of PCP, lower chlorinated phenols. Also it is known that there is often contamination of a PCP solution with PCDD's and PCDF's. These undesirable compounds can be formed when a sample of PCP is heated or exposed to light.

As a result of this fact, the extent of PCDD and PCDF formation and destruction in the Rayox process needed to be determined as this technology is already implemented in industry for the treatment of the waste water produced by wood treatment facilities.

In these tests, as mentioned earlier, an excess quantity of peroxide is used. Also the sample treated is a pure solution of high grade PCP in RO permeate. The result of this is that the determination of pseudo first order rate constants in terms of the degradation of the PCP, PCDD, and PCDF is possible, where first order kinetics are present.

EXPERIMENTAL:

Tests, for the most part were conducted in the same manner. A 1 ppm solution of 99% PCP in RO permeate was prepared. 12 L of this solution was pumped into the reactor and recirculated for five minutes to ensure homogeneity. During the first minute of recirculation the pH of the solution was adjusted to the desired value. For basic pH's NaOH was used and for acidification HCl or H_2SO_4 was used.

Once the equilibration period was complete a 500 mL and a 1 L sample were collected. At this time the UV lamp was engaged and during the thirty second or so window in which the lamp reached operating conditions the peroxide was added so as to achieve a 10 ppm concentration.

Samples for PCP analysis (500 mL) were collected at 0.5, 1, 2, and 5 minutes while samples for dioxin and furan analysis were collected at 1, and 3 hours.

PCP samples were analyzed by first performing solvent-solvent extractions using three 2 minute rinses with dichloromethane. The sample was then evaporated to almost dryness at which time the sample was transferred to hexane. All samples were then evaporated to 1 mL and injected onto a Hewlitt-Packard gas chromatograph which utilized a DB-1 capillary column and an electron capture detector. Area counts were then normalized with respect to the initial area count and plotted against time.

PCDD's and PCDF's were analyzed for by the Chemistry Division of Environment Canada at the River Road Environmental Technology Centre according to GC/MS standards using a 30 m DB-5 column installed in a Finnigan 4500 gas chromatograph.

RESULTS/DISCUSSION:

The optimum pH for the destruction of PCP, using H_2O_2 as the oxidant, was slightly acidic, in the pH 6.0 to pH 7.0 range, where HCl was used for acidification. Under these conditions it was found that the concentration of the PCP was reduced by greater than 99% in five minutes, (see GRAPH 1 in Appdx.)

PCP was found to degrade according to first order kinetics. The pseudo-first order rate constant for the disappearance of PCP at the optimum pH was found to be (1.6 +- 0.1) min^{-1}, or a half life of 25.7 s, (see GRAPH 2 in Appdx.).

When H_2SO_4 was used for acidification, the concentration of PCP was reduced to greater than 99% of the original part per million, as was the case when HCl was used.

The optimum pH for the destruction of PCDD's and PCDF's was found to be slightly alkaline, in the pH 7.0 to pH 7.5 range. At this pH not only did the PCDD's and PCDF's degrade fastest (see GRAPHS 3 & 4 in Appdx.), but their initial production was minimized, (see GRAPH 5 in Appdx.).

The total toxic equivalency of the sample solution was found to decrease to greater than 99% of its original value in one hour in the optimum pH range (see GRAPH 6 in Appdx.). One hour was also required for the removal of more than 99% of both the PCDD and PCDF congeners, (see GRAPH 3 & 4), where the OCDD congener was found to be the most stable to oxidation.

The experimental rate constant for the disappearance of the total toxic equivalency was found to be pseudo-first order under the optimum pH conditions, (see GRAPH 7 in Appdx.). The value of this rate constant was found to be (6.9 +- 0.1) hrs^{-1}, or a half-life of 6.0 min.

Under the extremes of pH, the degradation of the PCDD's and PCDF's were seen to deviate from simple first order kinetics. That is, the concentration was found to increase as the reaction co-ordinate increased. This was apparent from GRAPHS 6 & 7 where the degradation curves were not simple exponentials.

Upon consideration of what congeners were formed to make up the total toxic equivalency it was found that TCDD never formed, while the P5CDD congener formed often. This was an indication that the P5CDD congener was unstable, and readily oxidized, likely in a conversion from the dioxin structure to diphenylethers, or simple aromatics, possibly chlorinated phenols, before TCDD could be formed.

Similarly, it could be seen that the P5CDF, and the TCDF congeners were never formed while the H6CDF congener formed often. Therefore the H6CDF congener was the most unstable to the process, and the dibenzofuran structure was likely destroyed when this congener was formed.

SUMMARY:

In general then, it was found that for the treatment of PCP solutions in the concentration range of 1 ppm, a slightly alkaline pH of 7.5 or so was desirable. At this pH the destruction rate of the PCP was not significantly compromised, a residence time of only five min., and an environment where PCDD's and PCDF's were unstable to the Rayox enhanced oxidation process was found.

The TCDD, P5CDF, and the TCDF congener were all found to never form which indicated that the P5CDD, and H6CDF structures were unstable, and readily oxidized.

A residence time of one hour was determined to be sufficient to reduce the TLTEQ by greater than 99 %. A residence time of three hours was required to completely remove all PCDD, and PCDF that were produced by the reaction of PCP.

TABLE 1: PCDD/PCDF Data Obtained at pH 7.5 by GC/MS

TIME hrs	Quantity	[ ] pptr	Norm[ ]	ln Norm[ ]
0	TLPCDD	74.5	1.0	0.0
	TLPCDF	0.26	1.0	0.0
	TLTEQ	0.476	1.0	0.0
1	TLPCDD	0.48	0.0091	-5.04
	TLPCDF	0.0	0.0	u
	TLTEQ	0.001	0.002	-6.90
3	TLPCDD	0.0	0.0	u
	TLPCDF	0.0	0.0	u
	TLTEQ	0.000	0.0	u

* u refers to an undifinable quantity

TABLE 2: Results Obtained Under Optimum pH Conditions

Compound	Optimum pH	Residence Time	% of Original	Rate Constant	Half Life
PCP	6.0 - 7.0	5 min	< 99	1.6 min^{-1}	25.7 s
TLTEQ	7.0 - 7.5	1 hr	< 99	6.9 hrs^{-1}	6.0 mi

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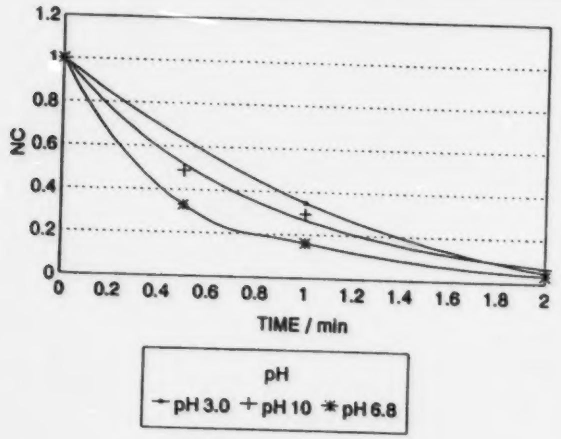
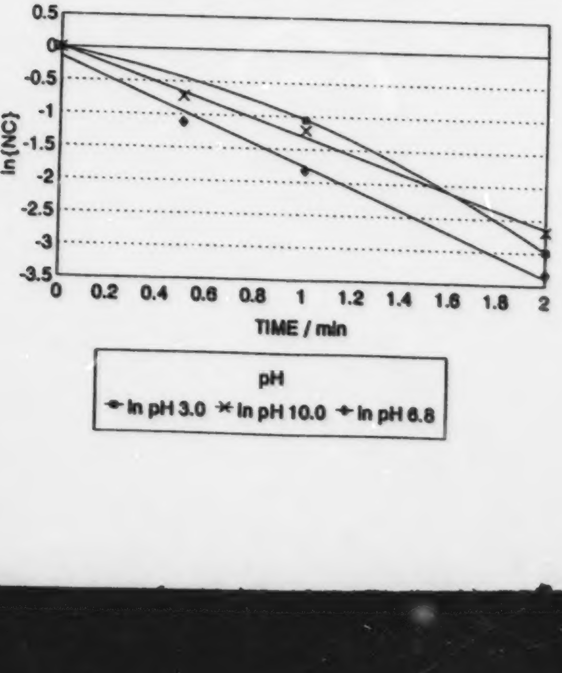
5) Seguin, N., "Domtar Wood Preserving Waste Water Testing", Unpublished, 1990.

APPENDIX

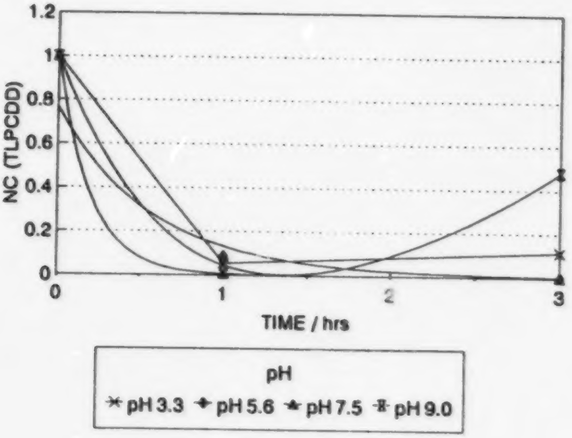
GRAPH 1: Normalized Concentration (NC) of PCP vs Time at Various pH's



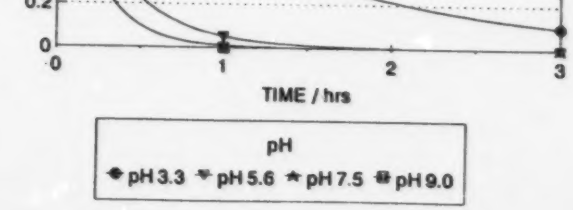
GRAPH 2: ln{Normalized Concentration} of PCP vs Time at Various pH's



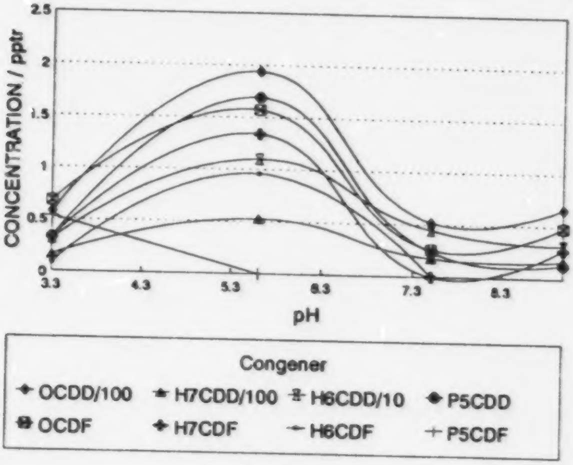
GRAPH 3: Normalized Concentration of TLPCDD vs Time at Various pH's



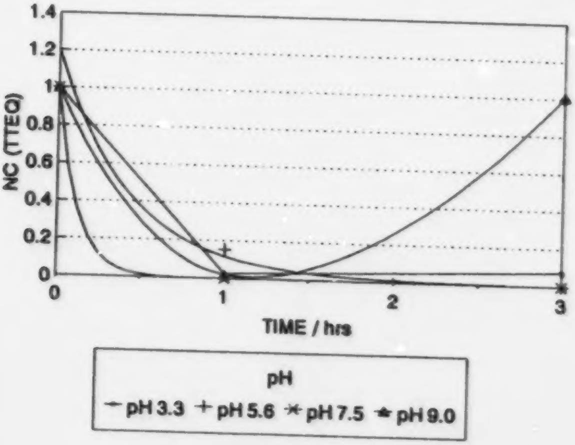
GRAPH 4: Normalized Concentration of TLPCDF vs Time at Various pH's



GRAPH 5: Initial Congener Concentration vs pH



GRAPH 6: Normalized Concentration of the TLTEQ vs Time at Various pH's



GRAPH 7: ln{Normalized Concentration} of the TLTEQ vs Time at Various pH's

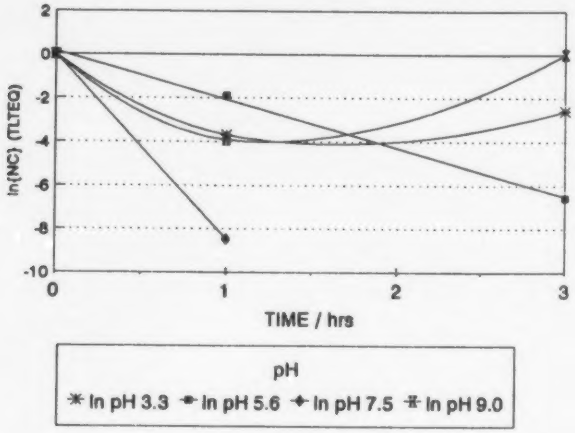
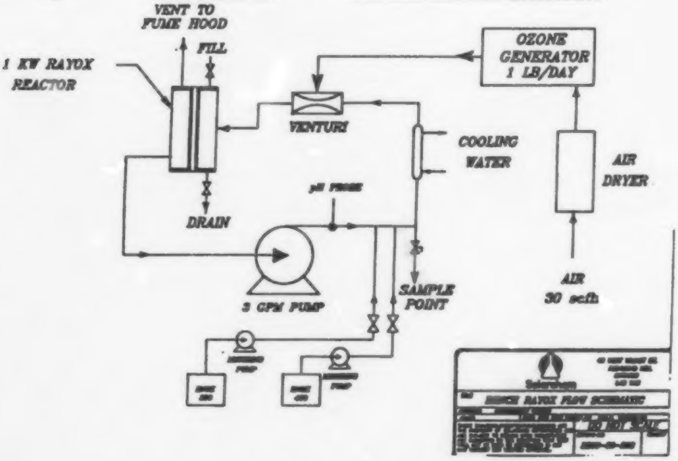


Fig. 1


VENT TO FUME HOOD
FILL
1 KW RAYOX REACTOR
OZONE GENERATOR 1 LB/DAY
VENTURI
COOLING WATER
AIR DRYER
pH PROBE
DRAIN
3 GPM PUMP
SAMPLE POINT
AIR 30 scfh
BENCH RAYOX FLOW SCHEMATIC
DO NOT SCALE

A STUDY OF MEMBRANE TECHNOLOGY AND ITS INTEGRATION WITH REMEDIATION EQUIPMENT

by

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ABSTRACT

This paper presents a series of tests conducted for the purpose of demonstrating membrane technology as a viable component in the field of site remediation and wastewater treatment technologies. Tests were conducted using Nanofiltration (NF), Reverse Osmosis (RO) and Microfiltration (MF). The effluents examined comprised of organic contaminants and inorganic contaminants. Results demonstrated that MF coupled with a PAA could be used as a softening system for process equipment in the field. NF coupled with polyethylene imine successfully treated process water generated from soil washing which contained an assortment of heavy metals. NF successfully treated a solution of 2,4,D producing a clean permeate and a concentrate which could be processed by enhanced oxidation technology. A solution matrix of organic compounds was treated by RO. The results demonstrated that a Filmtec high rejection membrane produced the best separation of an organic matrix. Conclusions are presented demonstrating how membrane technology can be integrated into site remediation equipment.

1.0 INTRODUCTION

The Environmental Emergencies Division (EED) demonstrates and evaluates various processes that treat chemical and oil spills[1]. The EED has worked with membrane technology since its inception in the early 1980's. During this period many trials were conducted using RO as a primary treatment process on contaminated ground waters[2]. The need to address environmental concerns has grown over the last decade and the technology required to deal with these concerns has also advanced. Stringent limitations on the amount of material that can be present in fluids destined for discharge are being monitored much more closely by regulatory bodies responsible for their implementation[3]. Conventional technology can not handle the requirements dictated by new regulations governing water quality in the 1990's and beyond into the next century.

The additional constraints that limit the use of conventional filtration systems has required industry and government to investigate specialized separation systems. Systems containing membranes possess the ability to separate compounds on a higher level. The ability to concentrate compounds and provide dischargeable and or reusable fluids is the great advantage that membranes possess over other technologies. With this intent in mind the EED conducted tests using membranes to supplement and compliment work being performed on systems that treat inorganic and organic wastes.

The first stage of investigation was conducted using a pilot scale MF unit owned by the EED. This test was performed to evaluate the ability of a polyelectrolyte to complex metals found in ground water. The polymerizing agent selected was polyacrylic acid (PAA). The use of these agents can produce results similar to UF or NF when dosed properly. The importance of producing positive results from this test is two fold. The product water would be softened and free of particulate thus providing boiler feed stock for the EED's steam stripper. A softened water supply would be produced without the use of anti scalents. The use of MF in this manner could provide a more cost effective way of producing boiler feed water in the field.

A test using NF to treat water contaminated with pesticides would be investigated. The problem associated with pesticide spills is the large volume of water and the small amount of pesticide which is contained in the collected water. Traditionally the EED would send its remediation equipment to these sites were it would process the collected fluid[4]. The NF would be utilised to concentrate this type of waste at two pH levels, one acidic and one basic. The test would determine if the NF could treat this fluid producing a clean permeate and a concentrate that would be further treated by the enhanced oxidation system possessed by the EED.

To compliment soil treatment technology that the EED is investigating NF would perform a series of tests on heavy metal solutions generated from the wash process. The first test would be to concentrate the soil wash waste without any modification other then slight acidification. The second test would utilize a polyelectrolyte that possessed an affinity for the heavy metals in the solution. The tests would be performed on two types of NF membranes which are commercially available. Utilization of NF in the soil wash process would enhance the treatment system by providing a significant volume reduction of the liquid waste, which at present, cannot be discharged.

The use of RO for concentrating waste fluids has been a focus of the EED in many of its projects. The testing of RO membranes would involve the concentration of hydrocarbons that are frequently encountered at waste sites that the EED had visited[5]. A series of tests on four RO membranes would be conducted for comparison purposes. As the membrane industry grows, applications that could not be performed in the past are being reviewed. New materials and diverse membrane properties coupled with lower cost(based on product flow) make RO a viable technology. The EED continues to recognize the importance of RO and continues to support its development for it is a technology of the future.

Foresight has shown that integratable process systems will be the most effective way to treat problems that occur from chemical and oil spills in our environment. No single technology can deal with the spill problem effectively. The public concern over our environment requires innovative engineers to produce the complete clean-up package. This is the way of the future and it must be addressed.

This paper presents results that demonstrate how membrane technology can be integrated into clean-up processes and the value it adds to the effectiveness of systems used for waste treatment.

2.0 METHODOLOGY

2.1 Microfiltration

Small scale testing involving the use of polyelectrolytes produced interesting results in complexing metals such as calcium, iron and manganese. A large MF unit was used to verify bench scale testing in the hope of producing similar results. The testing would involve coating the MF membranes with a dynamic layer of polyacrylic acid. Figure 1 illustrates this process.

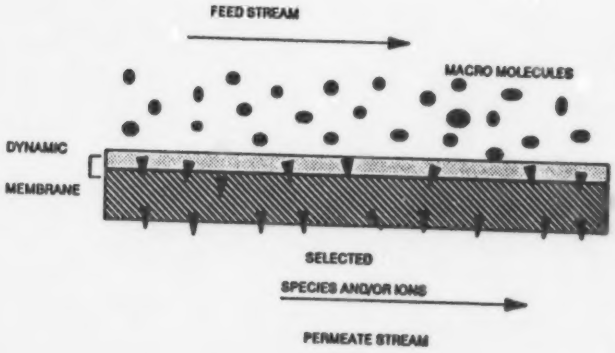

Figure 1 - PAA dynamic layer formation on the MF surface.

The molecular weight of the acid used for this dynamic layer was 4 million. A second acid of molecular weight 60K was used as the binding agent used to complex the metals in the test fluid. A solution of 200 L was made which contained 10 ppm PAA for the dynamic layer and 300 ppm of the 60K PAA to complex the metals. The solution was circulated at room temperature for two hours to ensure the formation of the dynamic layer on the surface of the MF. The test fluid comprised of local well water pH adjusted to 8.0.

The pilot MF system comprised of two ENKA MD 080 TP 2L polypropylene membranes each containing 43, 5.5 mm tubes. The particle size limitation for these membranes was .2 micron (nominal). The membranes operate on a cross flow principle where the feed flow travels on a parallel vector in relation with the surface of the tubes. The applied pressure forces the filtrate through the tubes were it is collected on the shell side as product water. The feed flow was set at 40 gpm at a pressure of 40 psi. The filtrate flow was monitored along with the rejection of the metals of interest. Analysis was performed by AA Spec. to determine the metal concentrations in the filtrate and the retentate. Figure 2 shows a general layout of a membrane system.

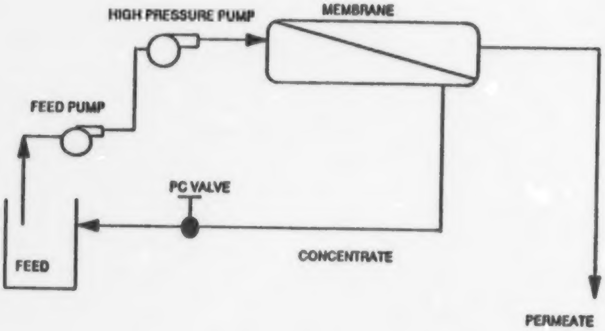

Figure 2 - Membrane configuration for batch concentration

Different runs were performed which included batch concentration at isothermal and non-isothermal conditions. These runs would evaluate how the polymer performed when subjected to different stress conditions (polymer breakdown) encountered from high speed pumps which are common on process equipment. Finally the solution would be acidified by the addition of HCl in an attempt to free the metals and regenerate the polymer.

2.2 Nanofiltration

The use of NF has been traditionally employed in the softening of hard water (high Ca and Mg content). Due to the nature of these membranes, they exhibit properties which favour their use over RO in the treatment of water contaminated with heavy metals from a soil wash process being developed at the EED. The high content of sodium would limit recoveries due to the high osmotic pressure that would be experienced if RO was employed. The ability of NF to reject anions and cations with multiple charges while having low rejections for single charged ions made NF a logical choice for the treatment of this wastewater.

The test solution was prepared based on results obtained during the precipitation and neutralization portion of the soil wash project. Using nitrate salts a 100 L solution was prepared which contained the following metals presented in Table 1.

	CONCENTRATION
METALS	ppm
SODIUM	10000
CALCIUM	1000
LEAD	4
IRON	1
COPPER	1
CADMIUM	1
ZINC	4

Table 1 - Feed solution used for heavy metal treatment.

This solution was processed in two stages. Stage one processed the feed in a batch mode with acidification to pH 5.0 by the addition of nitric acid. Stage two employed the use of a polyelectrolyte pH adjusted to 8.0 which was also processed in a batch mode. The polyelectrolyte used was polyethylene imine (MW 60000) produced by the Aceto Corp. under the name Epomine P-1000. The agent was added producing a concentration of 100 ppm in 100 L of solution. Figure 3 represents the basic building block of this polymer when it acts as a chelant.

from this test. Rejection values would be compared to determine the most effective operating conditions and which membrane performed the most favourably. No salt rejection tests were performed during the pesticide test.

2.3 Reverse Osmosis

Four types of membranes were tested on various compounds to determine their performance characteristics. The membranes chosen were thin film composites (TFC) all of spiral wrap configuration in a 2.5" x 40" size. The four elements are listed below:

1. FILMTEC SEA WATER
2. FILMTEC HR SEA WATER
3. DESAL 6
4. DESAL SEA WATER

The testing would be conducted on the following chemicals which are frequently encountered by the EED. A 100 L solution was prepared containing 1000 ppm ethylene glycol, 100 ppm toluene, 100 ppm tetrachloroethylene and 100 ppm of 2 chlorophenol. The test would be conducted at two different pH levels (5.0 and 9.0 using HCl and NaOH) for a comparison of the membranes performance on the solution matrix. The solution would be processed in a batch concentration mode in an effort to maximize recovery rates. All analysis would be performed by a GC using an FID and an ECD, no derivatization of the compounds would be performed and no salt rejections would be performed.

The parameters monitored for this test would include operating pressures, flow rates, temperatures and rejections. Recovery rates and permeate quality would also be examined to evaluate the success of RO to process this aqueous chemical matrix.

3.0 RESULTS AND DISCUSSION

3.1 Microfiltration

Results from the MF test followed the same trends as the work conducted during the bench scale testing. The drop in filtrate flow was rather large after the PAA had started to form a dynamic layer. The flow reduction occurred over a twenty minute period where a three fold decrease in the filtrate was observed. The filtrate flow stabilized at 8.0 L for the duration of the run. During the layer formation test the temperature ranged from 10 deg. C to 25 deg. C. Figure 5 graphically represents the flow degradation over time during the formation of the dynamic layer.

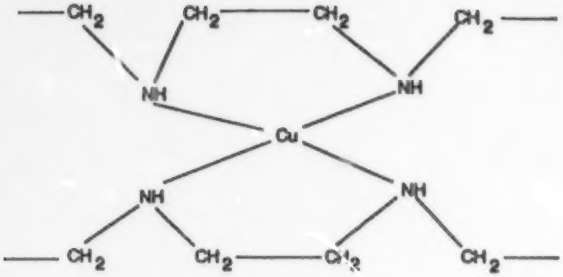

Figure 3 - Polyethylene imine structure.

The membranes used in this test were a Desal 5 and a Filmtec NF70. Both these membranes were of a spiral wrap configuration with dimensions of 2.5" x 40". In each test the flow rate, temperature and pressure were monitored and the metal analysis was conducted by an AA Spec.

A second series of tests was conducted employing the Desal 5 and the Filmtec NF70. In this test, the pesticide 2,4 Dichlorophenoxyacetic acid (2,4, D) was processed in a batch concentration mode. The test would be performed at two different pH's, one at 3.0 and one at 10.0. The agents used to modify the Ph of the test solution were Hcl and NaOH. By changing the pH of the solution the chemistry of the 2,4, D would also change, ie the sodium salt of 2,4, D should exhibit much higher rejections then its acid counterpart.

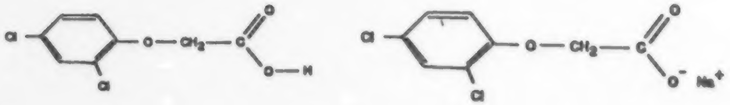

Figure 4 - a: 2,4, D pH 3.0. b: 2,4, D pH 10.0.

A 100 L solution was prepared in which 5.0 g of 2,4, D was added to produce a starting concentration of 50 ppm. The parameters monitored during the test were flow rates, operating pressures and temperatures. Recovery rates and permeate quality were determined by analysis on a GC using an ECD rather than an FID detector for greater accuracy. All the samples from this test were derivatized to give higher detection limits required for the permeate produced

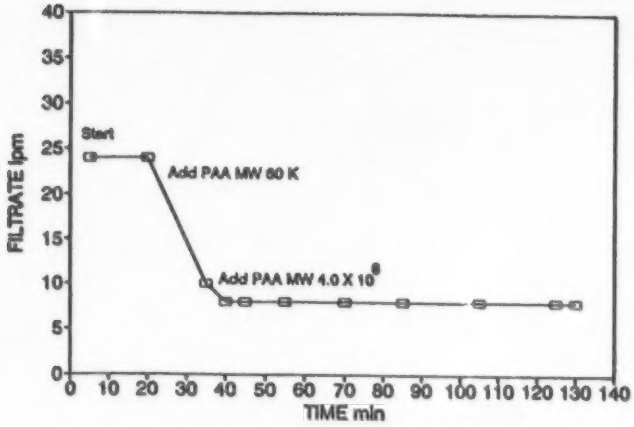

Figure 5 - Dynamic layer formation on the MF.

The time allocated to form the dynamic layer was sufficient based on Figure 5 and the batch concentration cycle was commenced. During this run the filtrate flow dropped from 8.0 L to 1.0 L. A volume reduction of approximately 80% was achieved. The pH adjustment after the 100 minute mark showed a dramatic filtrate increase as the metals were released back into solution and the resulting flow returned back to its original value of 8.0 L. The temperature fluctuation from start to finish during this phase of the test ranged from 23 deg. C to 28 deg. C. Figure 6 represents the batch concentration results of the run and the polymer regeneration process.

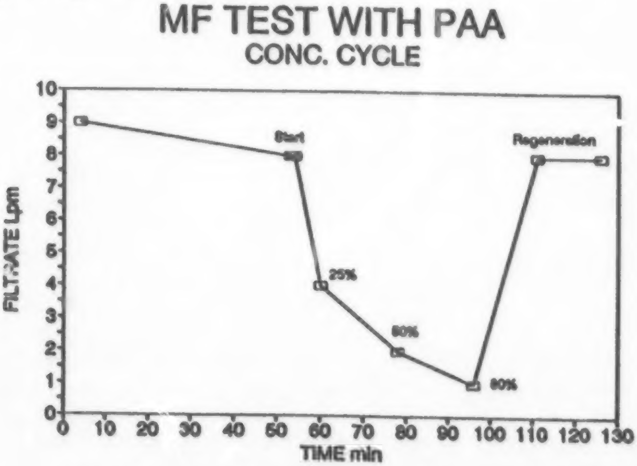

Figure 6 - Batch concentration cycle using MF.

The most interesting data to come from this test was the rejection of certain metals found in the ground water. The polymer had a high affinity for calcium and strontium which produced increasing rejection values as the run proceeded. The rejection values peaked at approximately 90% for both of these metals. The acidification of the feed was performed at the 240 min mark and within 20 minutes the rejection had dropped back to 0% as the metals were released from the polymer and the dynamic layer ceased to function. Figure 7 illustrates the rejections observed during the run.

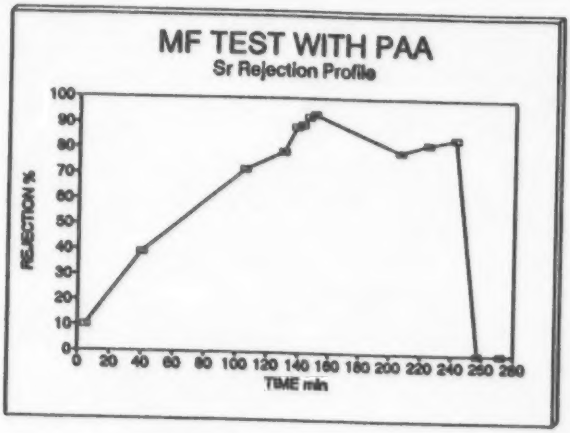

Figure 7a - Strontium Rejection.

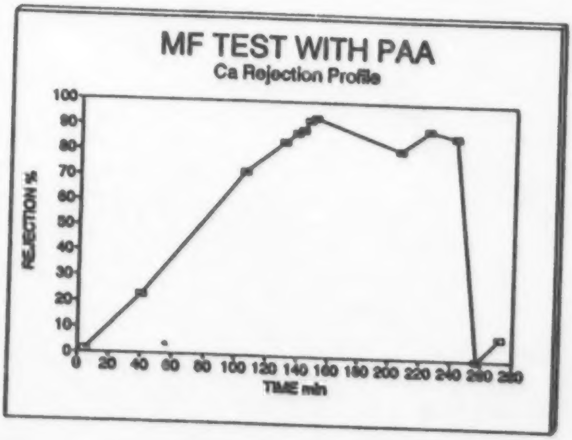

Figure 7b - Calcium Rejection.

Figure 7 - Rejection profile during the MF test.

The results for the stress test on the polymer was favourable. The polymer exhibited no observable breakdown during isothermal and non isothermal conditions. The isothermal test produced rejection results between 95 and 96 percent at 21 deg. C. The non isothermal conditions produced an average rejection of 96% between 21 deg. C and 38 deg. C. The rejection tests were carried out on calcium since it was the major constituent (40 ppm) in the feed water.

The implications that arise from this work employing polymers and MF to produce in-situ boiler water are significant. A realizable cost savings is achievable . The use of ion exchange beds is not a practical method to produce softened water in the field. Traditional use of RO and more recently NF use higher operating pressures ranging from 400 to 800 psi. The significant drop in flux is a concern when using MF for if a large volume of water is required, the added cost of modules might not offset the use of NF or RO.

A valid relationship can be established if the flow rate is compared using surface area as a basis. The MF produced product at a rate of 1.0 l/min m^2 when employing the PAA at 40 psi giving an average rejection of 96%. A NF would produce 0.68 l/min m^2 at 300 psi giving an average rejection of 98.5%. Both the above noted rejection values are based on calcium.

The advantage of the polymer system over NF can be realized in that the tubular MF is less likely to experience any more fouling effects while the NF would experience additional flow reductions due to the foulants that would come in contact with the surface of the membrane. The speed at which a dynamic membrane can be removed from the surface of the MF is much shorter then the required cleaning time that NF would require when used in the field. The polymer although not toxic can be reclaimed by acidification followed by ultrafiltration thus reducing the amount that would have to be employed in a field trial.

Future work should be performed on the pilot unit to optimize the molecular weight of the polymer and the type of polymer that would improve the characteristics of the system. The use of MF coupled with polyelectrolytes has potential in other applications such as reclaiming heavy metals, detoxification of waters containing radionuclides and the selective removal of material such as the fractionation of mono and multi charged metals. By the nature of this work, dealing with a simple softening technique, it hoped that the concepts can be further investigated to maximize the use of this coupling effect of polymer chemistry and membrane technology.

3.2 Nanofiltration

3.21 Heavy Metals

Data obtained from the Desal 5 test without the polyelectrolyte indicated that the rejection values of the heavy metals ranged between 74% to 95%. The rejection percentage increased as the concentration increased with the maximums ranging between a ratio of 2 to 4. Rejection values for calcium and sodium are representative of the properties of the test membrane used in this portion of the project.

The permeate by design would have a high sodium nitrate content due to the nature of the wash solution and the neutralization agent employed in the soil wash project. The ability of the Desal 5 to fractionate the heavy metals from the solution was achieved with a good degree of success.

The temperature was maintained between 23 and 25 deg. C producing operating pressures between 180 and 260 psi. Recovery percentages obtained peaked at 86% with a minimal effort to maintain the maximum permeation rate of 1.6 l/min. Table 2 summarizes the test results from this run.

REJECTION VALUES OBTAINED FOR TEST METALS

METAL	INITIAL CONC. (ppm)	RECOVERY	50	67	75	86
Pb	3.83		98.5	98.5	98.5	98.5
Na	12000		9.5	28	10.4	8.2
Ca	1660		99.9	99.9	99.8	99.8
Zn	3.87		90	92	91	89
Cu	0.88		74	82	83	84
Cd	0.91		83	85	86	85
Fe	0.5		80	93	95	94

Table 2 - Desal 5 results without polymer.

Data produced from the Desal 5 test using Epomine 1000 gave excellent results for heavy metal rejections. The rejections ranged between 91.6% and 99.9% for the heavy metals at various recovery stages during the batch. The agent also affected the rejection of sodium and calcium in a negative manner. The drop in rejection was due to the agent interacting with the membrane surface and modifying its charge character. The agent has no affiliation for both these metals and thus they passed through the membrane with greater ease. The lack of pressure increase in this test verifies the passage of the salts producing a lower osmotic pressure when compared to the previous test where most of the calcium and more of the sodium stayed on the concentrate side of the membrane.

During this test the pressure ranged from 168 psi to 185 psi and the temperature ranged between 18.9 to 22.2 deg. C. Recovery rates during this test reached 95% or a concentration factor of 20 while maintaining a permeation rate of 1.6 l/min. The agent experienced some physical changes between 90 to 95 percent recovery. The feed became effervescent and cloudy at these high recoveries. This phenomena could be explained due to the polymer agent, being highly rejected by the membrane, exhibited surfactant properties at these concentration levels. Table 3 presents the results of this test.

REJECTION VALUES OBTAINED FOR TEST METALS						
METAL	INITIAL CONC. (ppm)	RECOVERY	50	75	90	95
Pb	4.97		97.8	98.4	99.1	99.2
Na	11790			0		0
Ca	563			80.5		83
Zn	3.61		99.6	99.7	99.9	99.9
Cu	1.19		91.6	99	99.5	99.7
Cd	1.2		97.9	98.6	99.3	99.5
Fe	1.12		91.4	91.4	94.2	95.4

Table 3 - Desal 5 results using Epomine 1000.

Results obtained from the NF70 test produced rejection values ranging from 72% to 98% for the heavy metals without the use of a polymer agent. During the concentration of the solution the rejection values did not differ greatly from 50% to 90% recovery. The rejection of sodium was in the 27% range which produced operating pressures between 135 psi and 165 psi. The temperature ranged between 24 deg. C and 35 deg. C during the batch while maintaining a permeation rate of 1.6 lpm.

The use of the NF70 with Epomine 1000 produced increased rejections for all the metals in the test solution. The increase was significant for sodium and lead in which an increase of 20% was observed. The operating pressure during the concentration cycle ranged between 175 psi and 195 psi while maintaining a permeation rate of 1.6 lpm. The temperature ranged between 23 deg. C and 35 deg. C. Table 4 summarises the testing of the NF70.

TEST CONDITIONS	METAL	Na	Ca	Cu	Cd	Pb	Fe	Zn
INITIAL CONCENTRATION		5940	380	0.81	1.43	2.53	1.18	3.34
TEST 1 NO POLYMER								
25%		30.9	95.7	90.5	93.7	79.2	92.8	94.8
50%		28.4	95.9	93.1	94.0	78.1	92.9	94.7
75%		28.9	95.5	85.9	94.0	72.0	94.0	95.0
90%		21.0	95.5	88.8	94.9	72.2	96.1	97.8
TEST 2 WITH POLYMER								
25%		50.7	97.9	79.2	98.9	98.4	89.2	96.0
50%		38.9	97.6	83.0	97.8	98.1	90.5	96.9
75%		38.8	97.8	88.1	98.4	98.9	93.3	97.7
90%		38.1	98.6	93.3	98.9	98.5	96.7	98.4

Table 4 - NF70 batch concentration test results.

After examining the results of both NF membranes the most notable variable is the sodium rejection. The best conditions for producing a fractionated stream occurred when the Desal 5 was treated with the polyelectrolyte. High rejections of the heavy metals coupled with 0% rejection of the sodium was desired and achieved during this portion of the testing. The operating pressure for this system with a 90% recovery was only 185 psi at 23 deg. C.

3.22 Pesticide test - 2,4,D

Results from the test using the NF70 at a pH of 3 indicated that the rejection of 2,4, D was low. Values ranged from 1% to 42%. This low rejection can be explained by two reasons. The operating pressure was low for the duration of the run ranging from 75 psi to 80 psi which would not allow the membrane to compact. The second reason is due to the chemistry of the compound in which the carboxylic acid group was the predominant form present in the solution. The flow rate was maintained at 1.6 lpm between a temperature range of 22.8 deg. C and 32.2 deg. C.

The results obtained from the pH 10 run demonstrated significant improvement in rejection values. The rejection of 2,4, D ranged between 94% and 98%. The chemistry of the salt form of the pesticide aided in the improved rejections even though the operating pressure dropped to 50 psi for most of the run. The temperature of the run ranged between 28.9 and 37.2 deg. C. The flow rate was maintained at 1.6 lpm for most of the run.

The test results from the Desal 5 under acidic conditions produced low rejection values. The rejections ranged from 7% to 69% during the run. The temperature ranged from [illegible].8 to 26.7 deg. C with a pressure difference ranging from 105 psi to 80 psi. The maximum rejection value (69.79%) was obtained at 50% recovery. The flow rate was maintained at 1.6 lpm during the run.

Results from the Desal 5 under basic conditions produced higher rejection values for the 2,4, D. The rejections ranged between 97% and 99% with a maximum rejection (99.48%) obtained at 50% recovery. The operating pressure ranged from 105 psi to 90 psi between the temperatures of 16.7 and 27.8 deg. C at a constant flow rate of 1.6 lpm. Table 5 summaries the results of the NF test.

REJECTION RESULTS USING NF ON 2,4, D.

MEMBRANE	RECOVERY	25%	50%	75%	90%
NF70	pH 3	11.99	(24.53)	42.07	1.27
	pH 10	94.37	97.42	95.88	98.56
Desal 5	pH 3	7.28	69.79	58.59	53.96
	pH 10	99.05	99.48	97.93	98.71

Table 5 - Data summary of NF test for both test membranes.

The results for the NF test indicated that performing the separation was not effective at low pH levels. The use of either membrane under basic conditions would perform adequately at low pressures and moderate temperatures. The concentrated solution could be processed by enhanced oxidation for further treatment. The basic nature of the NF concentrate would save the on cost for pH adjustment usually performed on feed solutions before the oxidation process is initiated. High recoveries with high rejection values make NF an ideal membrane process to compliment treatment technology for this type of waste.

3.3 Reverse Osmosis

The performance of the RO membranes to separate and concentrate an organic matrix showed promise. The best performance was exhibited by the FT30 SW membrane for flow rate and operating pressure. The membrane produced 1.6 lpm at an operating pressure of 550 psi between 21.1 and 25 deg. C. The lowest flow rate was exhibited by the Desal 6 which produced 0.7 lpm at 600 psi between the temperatures of 16.1 and 37.8 deg. C. The remaining two membranes (Desal SW and the FT30 SW HR) produced flow rates between 0.8 and 1.2 lpm at 600 psi. It is important to note that the operating pressure and the flux rate are not the only consideration when membranes are employed in site remediation situations. The productivity usually does not play an important role in the selection process, rather the ability of the membrane to reject certain compounds exhibits more importance.

The rejection performance for the four membranes was evaluated on how each membrane rejected the compounds in the solution as the batch was processed. The rating system was based on a one to four scale with the lowest summation indicating the best over all rejection performance for the test. Analytical problems for the ethylene glycol prevents its evaluation to be included in this paper. Table 6 presents the rating of the four membranes used in this test.

Membrane	Compound	Tcluene	TCE	2 Chloro Phenol	Total
Desal SW	25%	1	3	1	5
	50%	2	3	2	7
	75%	2	1	1	4
	90%	3	2	1	6
					22
Desal 6	25%	4	4	4	12
	50%	4	4	4	12
	75%	4	4	4	12
	90%	4	4	4	12
					48
FT30 SW	25%	3	2	3	8
	50%	3	2	3	8
	75%	3	3	3	9
	90%	2	3	2	7
					32
FT30 SW HR	25%	2	1	2	5
	50%	1	1	1	3
	75%	1	2	2	5
	90%	1	1	3	5
					18

Table 6 - RO membrane performance evaluation.

Rejection results show that each membrane performed well at certain points in the run. The exception was the Desal 6 which had the lowest rating of the four membranes. This is not to say that the membrane did not work but rather as a comparison, it did not produce the rejection levels that the other three membranes demonstrated. The rejection summary for the RO testing is presented in Table 7.

Membrane	Compound	Toluene	TCE	2 Chloro Phenol
Desal SW	25%	99.1	99.2	95.0
	50%	97.9	99.4	93.5
	75%	95.9	99.9	95.7
	90%	95.2	99.8	97.6
Desal 6	25%	91.3	95.2	83.0
	50%	91.5	95.8	85.3
	75%	91.1	95.9	87.7
	90%	88.4	95.6	88.7
FT30 SW	25%	97.9	99.9	92.1
	50%	97.1	99.8	91.6
	75%	95.6	99.6	91.1
	90%	95.3	99.4	96.3
FT30 SW HR	25%	98.8	99.9	93.3
	50%	98.6	99.9	93.7
	75%	98.0	99.8	93.5
	90%	98.3	99.9	93.6

Table 7 - Rejection results for the four RO membranes.

The use of RO in conjunction with other remediation technology will continue to be an important component in the treatment of contaminated water. The ability of RO to process inorganic contaminants is widely accepted as a polishing system. The use of RO to close the process loop in non traditional applications was applied in this project to gather data on how effective it would be on frequently encountered organic compounds. The integration of RO with other treatment technologies such as enhanced oxidation and steam stripping would compliment their respective roles in the clean and treat process. Additional work would have to performed to optimize a combined unified treatment package. Figure 8 illustrates a proposed process train to treat ground water contaminated with organics.

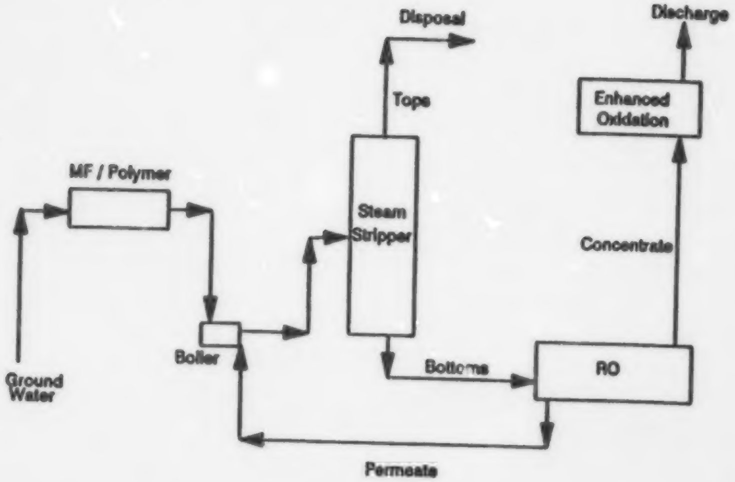

Figure 8 - Potential treatment system.

4.0 CONCLUSIONS

The coupled use of MF and polyelectrolytes (PAA) produced water with a calcium reduction of 90% at 50% recovery. The coupling effect produced lower flux rates comparable with nanofiltration but did so at a much lower pressure (40 psi). The use of MF would provide a softened water supply suitable for the steam stripper operated by the EED for site remediation.

The integration of NF in soil remediation technology targeted at heavy metal removal was achieved. The best results were obtained with a Desal 5 coupled with polyethylene imine. A 90% volume reduction was obtained producing a reusable effluent as a fertilizer. The integration of NF would provide a closed loop (for the aqueous phase) in the soil treatment system being developed by the EED.

The successful removal of 2,4, D was achieved by NF under basic conditions. The two NF membranes tested produced similar results and either would suit this application. A volume reduction of 90% was achieved which produced a concentrated solution that could be processed by an enhanced oxidation system operated by the EED. The NF membranes under acidic conditions would not produce the separation required for this treatment system.

The results from the RO testing demonstrated that the highest productivity was achieved by the Filmtec sea water membrane. This membrane operated at lower pressures (550 psi) and produced rejections between 91% and 99% for three of the four organic compounds in the solution. The use of RO continues to be the only effective method of separating compounds to produce effluent in the low ppb range. The concentrate from the organic matrix could be sent to the enhanced oxidation system for further treatment. The bottoms from a steam stripper which would contain most of the non volatile organic compounds could be treated by RO and the concentrate would be treated by enhanced oxidation. This combination of membrane technology with other remediation equipment would close the waste loop in a more efficient manner thus maximizing the use of treatment technology in the field.

More study into the coupling effect of polymers and membranes is required to optimize the benefits that could be realized from their combination. Due to a lack of time not all the new developments in membranes and their potential integration into systems could be examined but work should continue to explore this avenue.

Acknowledgements:

The author wishes to thank the EED at Environment Canada for the use of its equipment and resources. A special thanks is noted for Dr. Velicogna whose assistance in the sample analysis was greatly appreciated.

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REMEDIATION OF SOIL CONTAMINATED WITH HEAVY METALS AND PCB's

by

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ABSTRACT

The results of laboratory scale soil washing tests are presented. The remediation process included both mechanical and physico-chemical treatment of soil contaminated with lead, copper, zinc, cadmium and PCB's. The methods for the treatment process were determined. The outcome of the treatment studies of soil washing wastewater are discussed. A process train for the treatment of test soil has been recommended. Feasibility of solvent regeneration via membrane separation, after removal of PCB's via solvent extraction, has also been investigated.

INTRODUCTION

Soil contamination has become a serious problem and has attracted much attention in North America. Treatment of contaminated soil is used extensively in Europe and has become important in North America in the recent years[1]. The number of contaminated sites requiring urgent attention in Canada and United States is increasing which calls for efficient and cost effective treatment methods.

Environment Canada's Emergencies Engineering Division (EED) has recently conducted research on the methodology and the feasibility of soil remediation. The main objective of this study has been to develop and propose a process train for remediation of a soil contaminated with heavy metals and PCB's, along with the treatment of the wastewater resulting from the process. As far as PCB's are concerned, a preliminary study on the regeneration of the solvent after PCB removal via solvent extraction, using a membrane has been performed in this study. A suggestion on where the process train should include a PCB removal step has also been provided. Figure 1 demonstrates the general outline of the approach adopted in this study for the treatment of contaminated soil.

The site under investigation is a property of the Ministry of Transportation of New Brunswick which has been used as a scrapyard and storage for batteries and transformers. The soil is contaminated with PCB's and heavy metals such as copper (Cu), lead (Pb), zinc (Zn) and cadmium (Cd). The heavy metals are mostly in the form of metallic solids which exist in a wide range of sizes.

There are a wide variety of methods available for soil treatment. Unfortunately, a specific universal method does not exist, due to the diverse geological/physical characteristics of soil and nature of the contaminants contained in the soil matrix. Both the mineralogical characteristics and the metal concentration of the soil must be considered when evaluating methods for soil treatment.

The Canadian Council of Ministers of the Environment has recommended interim standards for environmental quality criteria for contaminated sites. The remediation criteria has set the acceptable concentration of metals for commercial and industrial sites at 20 ppm for cadmium, 500 ppm for copper, 1000 ppm for lead and 1500 ppm for zinc[2]. In order to meet these standards, different methods such as physical, mechanical, chemical and their combinations have been investigated and compared in the present study. Due to the non-homogeneous nature of the test soil, the results and efficiency of the treatment methods have been evaluated with respect to each sample tested.

Rinse waters resulting from the soil treatment process are highly contaminated with heavy metals at concentrations as high as several grams per litre. To meet environmental requirements, these metals must be removed before discharge into the environment. For this reason, any method applicable for treating waste water containing heavy metals can be used. A few established methods are: reagent precipitation, ion exchange, electrodialysis and solvent extraction. Reagent precipitation (via neutralization) has been chosen for its low cost and relative simplicity.

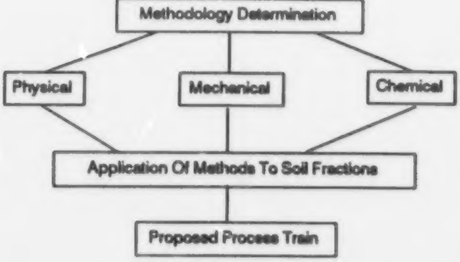
Soil Chracterization
Mineralogical Analysis
Soil Classification
Methodology Determination
Physical
Mechanical
Chemical
Application Of Methods To Soil Fractions
Proposed Process Train

FIGURE 1. General outline of the approach adopted for soil treatment.

PCB removal via solvent extraction results in an organic wastewater with high concentrations of PCB's. An effective, but perhaps not very energy efficient, method to recover the solvent with high recovery is distillation. The feasibility and possibility of membrane technology as a potential substitute for distillation has been investigated.

PROCEDURES

The details of the experimental conditions have been explained with the results. More details about the description and application of the methods listed below can be obtained from special literature in the areas of hydrometallurgy, mineral processing and wastewater treatment. The procedures and analytical methods used are as follows:

Soil Treatment

- dry classification;
- wet classification;
- attrition (wet and dry);
- acid leaching (AL);
- flotation;
- density separation (gold table/gravity table and air table);
- magnetic Separation;
- electrostatic separation.

Wastewater Treatment

- reagent precipitation;
- membrane separation.

Analytical Methods

- Scanning Electron Microscopy using Energy Dispersive X-ray Analyzer (SEM/EDX);
- digestion of the soil samples with aqua regia (1:3 v/v mix of 70% HNO_3 and 37% HCl);
- Atomic Absorption Spectroscopy (AA);
- Gas Chromatography (GC).

RESULTS AND DISCUSSION

In the search for the most efficient and effective method for remediation of the test soil, several different methods were performed and compared. Tests were carried out on the raw soil (without classification) and on the fine and coarse fractions of the soil. The methods used were chemical, mechanical, physical and their combinations.

Mineralogical analysis and dry classification

A mineralogical analysis of the soil sample was carried out by Mineral Science Laboratories at the Canada Centre for Mineral and Energy Technology (CANMET). Polished sections were prepared from each fraction of the soil and mineral species were determined via ore microscopy and electron microscopy. The general phase characterization and identification of metal carriers were mainly based on SEM/EDX[3]. The purpose of the analysis was to determine the physical characteristics of the soil, metal carriers and the physical form in which the metals appear (eg. silicates, salts, metallic solids). Figures (2 - 5) show the nature of the metallic particles and the soil matrix. The metal contaminants of major concern were lead, copper, cadmium and zinc. These metals mostly existed in the form of metallic solids. Lead and copper were abundant in all the fractions of the soil.

According to the mineralogical analysis, the average metal concentration of the soil sample was 21500 ppm Cu, 30 ppm Cd, 12600 ppm Pb and 3700 ppm Zn. Copper occurred as metallic copper (~95%), copper chloride (~2%), copper oxide, silicates and alloy. Lead was present as lead metal(~95%) covered with PbO and $PbCl_2$, small amount of lead chloride (~2%), oxide, sulphate, and silicates. Zinc occurred as $ZnFe_2O_4$, zinc metal, plus minor constituents of various complex silicate mixtures[3]. The analysis showed that 30% of the zinc is removable and the 70% in the form of silicates, which are already immobilized, were not considered as contaminants. It is therefore important to note that not 100% of each metal present in the soil is considered as a contaminant. The dry classification of the soil sample is presented in Figure 6 which demonstrates the size range of the soil particles in each fraction. The dry classification was performed using a sieve shaker and a set of sieves with mesh sizes of 0.038-15 mm.

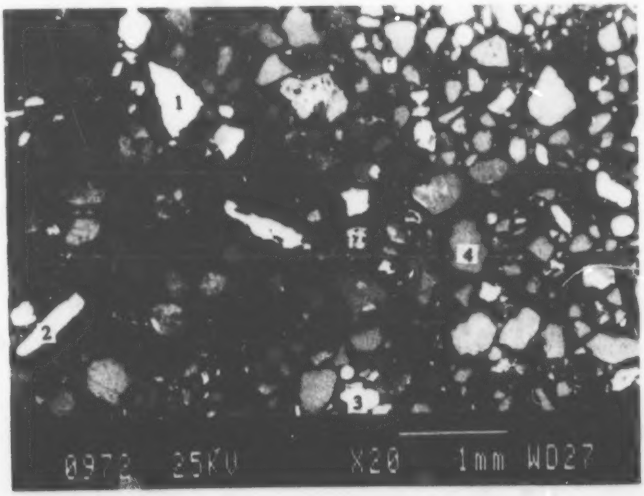

FIGURE 2. Backscattered electron micrograph showing the general mineralogy of the sample: 1- Fe_2O_3, 2- Cu metal, 3- Pb metal, 4- silicate[3].

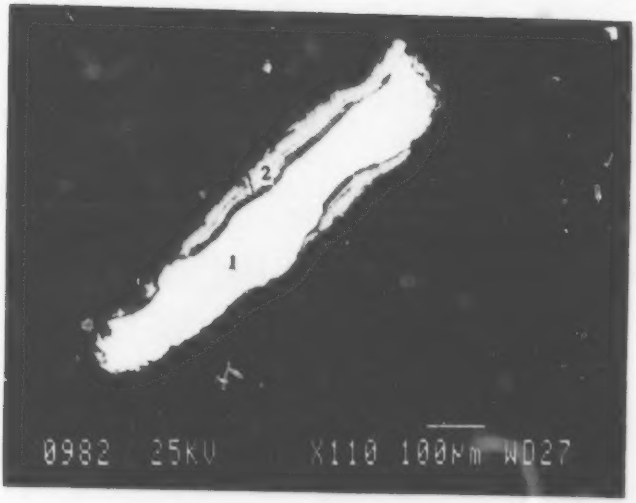
2
1
0982 25KV X110 100µm WD27

FIGURE 3. Backscattered electron micrograph showing the typical morphology of the Cu metal in the sample. 1- Cu metal, 2- Cu_2O.[3]

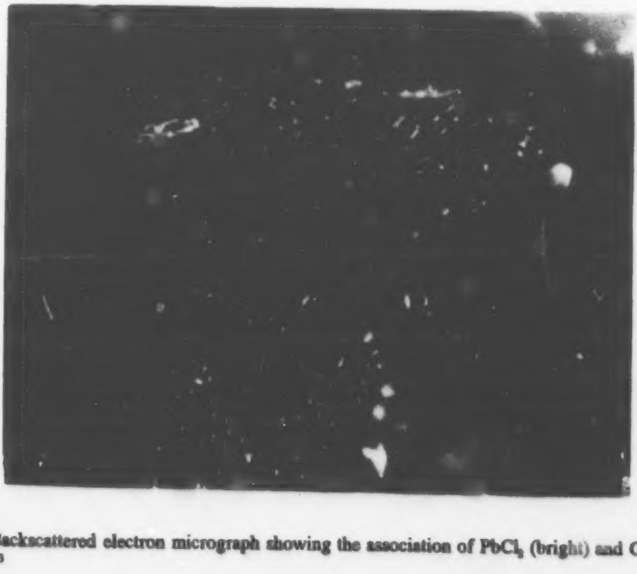

FIGURE 4. Backscattered electron micrograph showing the association of $PbCl_2$ (bright) and $CuCl_2$ (dark matrix).[3]

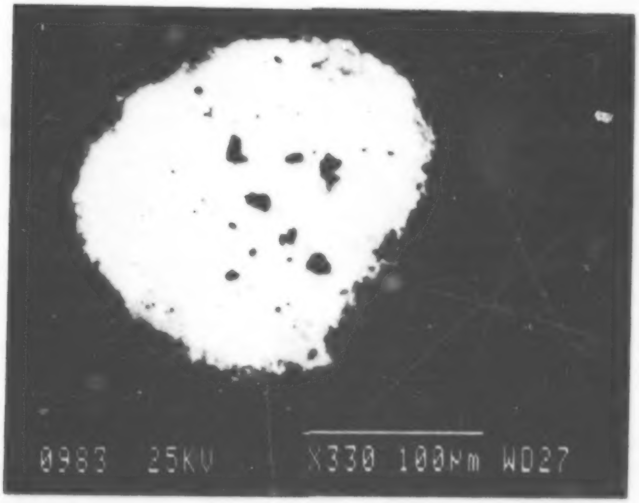

FIGURE 5. Backscattered electron micrograph showing the typical morphology of the Pb metal in the sample. The Pb metal is frequently rimmed by $PbSO_4$ or PbO; quartz (sand particles) is commonly present as inclusions in the Pb metal[3].

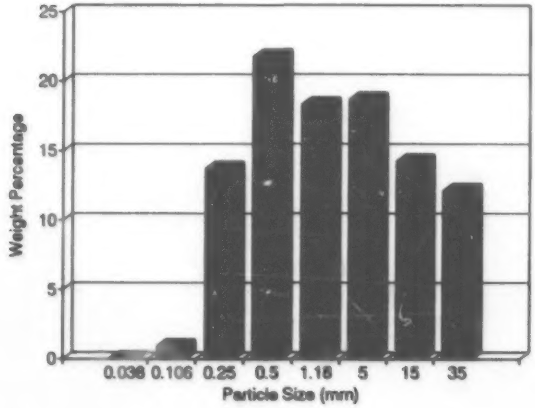

FIGURE 6 . Dry classification of the test soil.

Once the soil sample was classified into different size fractions, the metal concentration of each fraction was determined. The results of the fractional analysis of the test soil is presented in Table 1.

TABLE 1. Results of soil fraction analysis.

FRACTION SIZE (mm)	% METAL IN FRACTION			
	Cu	Cd	Zn	Pb
0.0 - 0.038	0.07	0.09	0.11	0.09
0.038 - 0.106	1.18	2.50	1.60	1.90
0.106 - 0.250	18.5	33.8	23.4	18.6
0.250 - 0.50	29.6	40.1	37.6	29.2
0.50 - 1.18	40.0	15.0	21.0	14.5
1.18 - 5	10.4	5.74	14.7	36.1
5 -15	0.16	1.46	0.98	0.25
15 - 35	0.05	1.24	0.73	0.06

Additional analysis showed that the surfaces of the lead and copper metal pieces were coated with chlorides and oxides[3]. This indicates that the metallic solids in the soil were not stable under certain climatic conditions (acid rain) and would leach from the soil into the water table.

Wet Classification

A wet classification of the test soil was carried out to determine which fractions of the soil had to be treated for the maximum removal of each metal and how each fraction should be treated to obtain this goal.

The treatment consisted of attrition of the test soil for 1.5 hrs (at a propeller speed of 920 rpm and 20°C) and wet classification of the slurry. A commercial detergent was added to one of the samples to observe the effect of a surfactant on the soil structure and the metal distribution in the sample fractions. For the wet classification of the slurry, a screening and horizontal shaking was carried out using a standard shaker table. The horizontal shake was brought to a halt slowly by the reduction of the shaking speed. The process produced four fractions. Each fraction was then analyzed for its metal content.

Large copper wires and solder-like metallic solids were observed in the soil matrix. In the 1.18-4.00 mm fraction complete separation of the metallic solids was observed. In the 0.50-1.18 mm fraction an abundance of small pieces of copper wire was observed without any separation from the soil matrix. This fraction was classified into magnetic and non-magnetic subfractions by a Rare Earth Permanent Roll Magnetic Separator. Each of the subfractions were then treated with an electrostatic separator. The electrostatic separator divided each of the subfractions into conductor, middling (the term middling is used for particles having a conductivity, intermediate with respect to that of conductor and a non-conductor) and non-conductors. The various fractions obtained were analyzed for metal content and the results are presented in Table 2. The distribution of metals in the various fractions is shown in Figure 7.

The effect of the surfactant produced an increase in the >0.50 mm fraction from 46% to 58% by weight. The surfactant weakened the forces binding the particles of all sizes together. These forces are adsorption forces, Van der Waals and London forces as well as hydrogen bonding between clay particles[4]. An increase in the removal efficiency of zinc, cadmium, copper and lead dust (in the 0.10-0.20 mm) resulted from the increase of the <0.50mm fraction obtained by using a surfactant.

Table 2 shows that the non-magnetic fraction contained 62% of total copper and 68% of total lead in the 0.50-1.18 mm fraction and the magnetic fraction contained 70% of total cadmium and 75% of total zinc. The non-magnetic fraction contained all the visible metallic solids. The electrostatic separation, therefore, did not make a noticeable difference and the magnetic separation was sufficient to reduce the amount of material that had to be processed. It should be noted that the soil should be completely dry and clean for the electrostatic separation to provide good results. The test soil particles were covered with a thin sheet of transformer oils which decreased the effectiveness of electrostatic separation. Satisfactory results may have been obtained, if the soil had been free of transformer oils.

TABLE 2. Metal distribution in the magnetic and non-magnetic sub-fractions of the 1.18-0.50 mm fraction.

FRACTION		%METAL			
		Cu	Cd	Zn	Pb
MAGNETIC	CONDUCTOR	18	20	26	37
	MIDDLING	14	34	30	7
	NON CONDUCTOR	7	17	18	12
NON MAGNETIC	CONDUCTOR	52	18	9	29
	MIDDLING	2	8	12	25
	NON CONDUCTOR	8	4	5	14

Other Mechanical Treatment

Further mechanical separation techniques were tried on the soil sample in an effort to determine the most effective separation which produces the minimum amount of waste. The soil was classified into four fractions after dry attrition. Results are presented in Table 3.

TABLE 3. Weight percentage of the soil fractions after dry attrition

FRACTION SIZE (mm)	%WT
>4.00	28
4.00 - 1.18	19
1.18 - 0.50	19
<0.50	34

The fraction >4.00 mm contained a substantial amount of solder-like metallic solids. The majority of the copper wire was observed to be in the range of 0.05-4.00 mm.

Half of the <0.50 mm fraction was subjected to wet attrition and flotation. The metallic solids in the post flotation slurry were then separated on a gold table according to density difference. The objective was to see what percentage of the sample, on the weight basis, would separate with the metallic solids. The flotation froth contained 23% of total copper, 99% of total cadmium, 18% of total lead and 45% of the total zinc which corresponded to 24% of the sample by weight.

The slurry was separated into table concentrate, table middling and table tailing using a Gold Table. These separations were based on density with table concentrate having the highest. The metallic solids were separated in the table concentrates being 18% of the total sample by weight. The table concentrate contained almost all of the metallic solids. The cylindrical shape of the copper wires interfered with the separation because the copper wires would roll down the table and separate with the middlings.

A portion of the <0.50 mm fraction was first passed though a 0.25 mm sieve. The fraction <0.25 mm had no metallic solids. The 0.25-0.50 mm fraction was then treated on an air table which also works on the principle of density difference. In the case of the air table the flow of air is upwards, unlike the gold table in which the flow of water is horizontal. The shape of the copper wires did not interfere with the separation when using the air table. The air table successfully separated the metals and concentrated them into 7% of the above fraction.

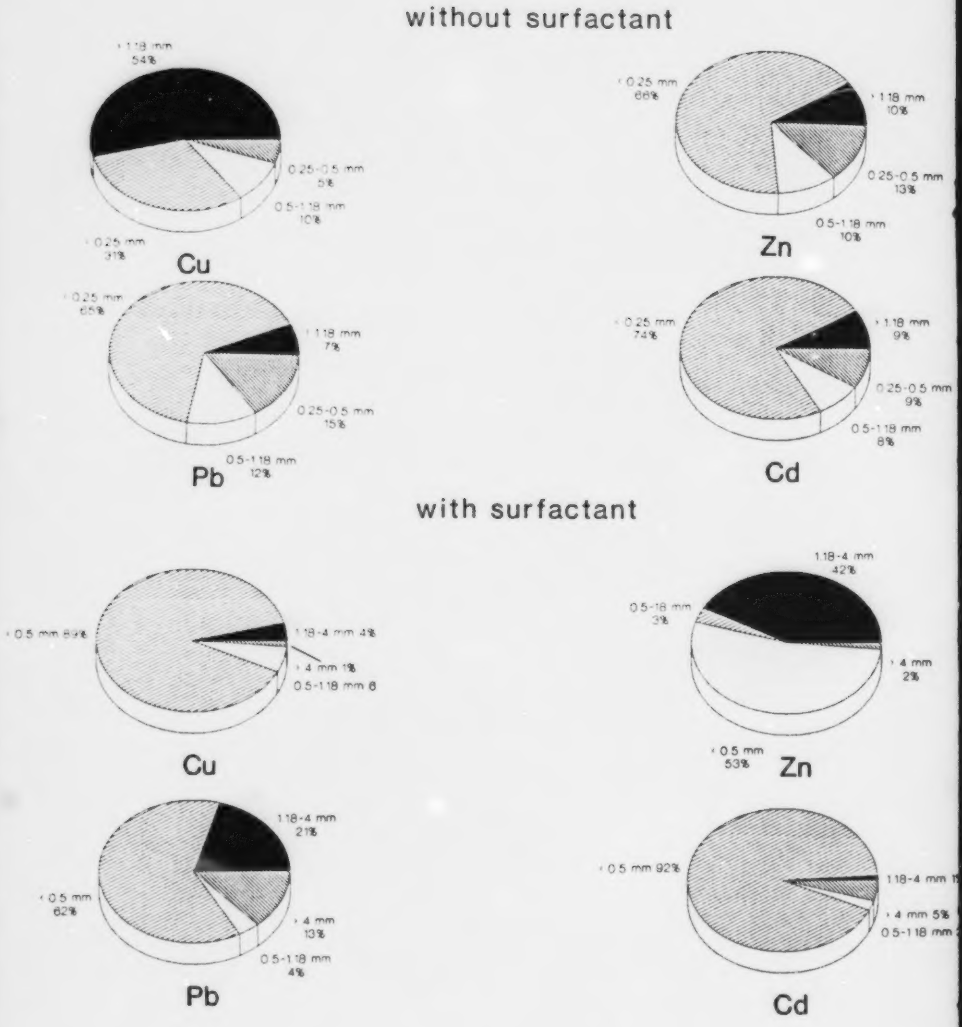

FIGURE 7. Metal distribution in the soil after wet classification, with and without the addition of surfactant.

The rest of the fractions were treated in the same manner. For every fraction treated the separation with the air table was more efficient. The air table was able to separate the metallic solids by concentrating them into less than 8% (as opposed to 18% when using a Gold Table) by weight of each of the samples treated.

The >4.00 mm fraction which contained a large amount of solder like solids, was crushed down to a 4.00 mm size. As a result of the crushing all the metals were flattened and completely removed by simple screening with a 4.00 mm mesh.

Acid Leaching

The acid wash was carried out at 20°C and the slurry mixed at 210 rpm for 3.5 hrs. The slurry was filtered and the sludge and filtrate obtained were analyzed for their metal content.

The soil fraction of < 1.8 mm was separated and leached with three different acids HCl, H_2SO_4 and HNO_3 at a pH of 1 in order to determine the most efficient acid for the process (Table 4).

TABLE 4. Results of soil washing with HCL, HNO_3 and H_2SO_4

ACID (0.1 N)	% REMOVAL			
	Cd	Cu	Zn	Pb
HCl	54	23	80	33
HNO_3	39	58	50	66
H_2SO_4	44	35	60	0

The most effective acid was selected based mostly on the recoveries that were achieved for Cd and Zn. This was due to the fact that AL was the key method for Cd and Zn removal. Cu and Pb removal were not the deciding factor in the acid selection because ~95% of these metals were in the form of metallic solids, which were removed using mechanical treatment.

From the three acids tested, HCl was selected for it's high Cd and Pb removal and relative low cost. It is important to note that a neutralization step should follow the acid leaching step and the combined effect of the AL and neutralization would

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The results in Table 6 demonstrate that temperature and pH during pre-treatment did not play an important role in the removal efficiency. It can also be seen that a substantial amount of the metals in the fine fraction has been removed. One can assume that the fine fraction (<1.18 mm) of the soil contains almost all of the zinc which can be removed by AL. Cadmium also exists mainly in the fine fraction of the soil and can be removed very effectively by AL.

TABLE 6. Results of wash at 20°C and 50°C.

TREATMENT	% REMOVAL							
	50°C				20°C			
	Cd	Cu	Zn	Pb	Cd	Cu	Zn	Pb
WATER WASH pH 7 (FINE)	71	60	64	75	43	67	63	75
WATER WASH pH 4.5 (FINE)	75	54	62	50	52	70	69	50
WATER WASH FLOTAT'N ACT. CARBON	-	-	-	-	52	61	46	75

Waste Water Treatment

In all the tests the wash water from attrition and the filtrate from AL had to be treated in order to be recycled or discarded. In case of discharge the interim standards set by the Canadian Council of Ministers of the Environment had to be achieved. The standards are listed in Table 7[2].

The wastewater treatment tests were carried out on 100 litres of solution which was based on the expected concentrations of the metals in the actual process wastewater. The samples were neutralized and the metals precipitated. The resulting liquid phase was treated with a membrane system.

Reagent Precipitation

Results of reagent precipitation are presented in Table 8. The concentration of major contaminants (Pb, Cu, Zn) dropped from several grams to several milligrams per litre. The concentration of Cd also decreased, except in the case of calcium carbonate treatment.

TABLE 7. Interim criteria for water

INORGANIC PARAMETER	PURPOSE		
	FRESHWATER/ AQUATIC LIFE (ppb)	IRRIGATION (ppb)	LIVESTOCK WATERING (ppb)
Cu	2-4	200-1000	500-5000
Cd	0.2-1.8	10	20
Zn	600	500	1500
Na	-	-	-
Ca	-	-	1000
Fe	300	5000	-
Pb	1-7	200	100

Satisfactory metal separation was not achieved for Cd (Figure 8). Iron can be separated from other components within the pH range 3-4, which produced the precipitation of approximately 90% of this metal. Copper, lead and zinc co-precipitated at pH 4-7, thus their separation from each other appears to be impossible.

Despite the fact that the initial metal concentrations were reduced by several orders of magnitude, the residual concentrations were higher than the discharge limits. Additional treatment is therefore required. To achieve discharge limits membrane technology such as a nanofiltration membrane could be used.

TABLE 8. Metals concentrations (ppm) in wastewater before and after neutralization

METAL	BEFORE TREATMENT (ppm)	AFTER NEUTRALIZATION TO pH 7 WITH (ppm):		
		NaOH	Na_2CO_3	$Ca(OH)_2$
Cu	6,540	4.81	1.13	45.0
Cd	7.44	0.30	0.35	6.20
Pb	930	1.24	3.84	12.1
Zn	1,140	16.3	11.3	-
Fe	10,970	4.52	2.32	2.13

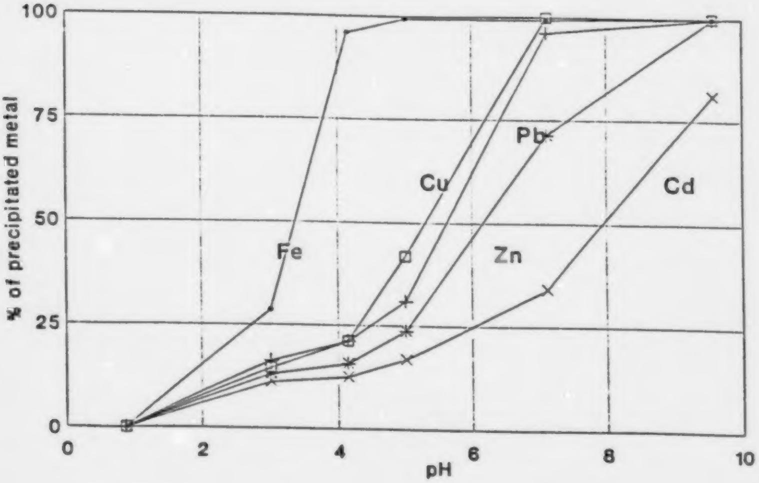

FIGURE 8. Results of the reagent precipitation of metals with NaOH

PCB's

The distribution of PCB's in different fractions of the soil was determined. In order to determine the PCB content of each fraction, the PCB's from a 10g sample was extracted and the concentration was determined by gas chromatography. A standard soil sample and a blank was run with each batch and the concentration of the actual samples was calculated with respect to the standard and blank. The extractions were carried out at 20°C and a 1:1 v/v Acetone/Hexane solvent system with a ~75% extraction efficiency. Figure 9 demonstrates the PCB distribution in the test soil.

The PCB analysis of the fractions of the soil after mechanical treatment showed that the metal wastes have a PCB concentration of 50-300 ppm, therefore, these metal wastes should be treated for PCB's before disposal. Figure 9 shows the distribution of PCB's in different fractions of the soil.

The PCB analysis of the fractions of the soil after mechanical treatment showed that the metal wastes have a PCB concentration of 50-300 ppm, therefore, these metal wastes should be treated for PCB's before disposal. Figure 9 shows the distribution of PCB's in different fractions of the soil. The figure shows that the major amount PCB exist in the <0.50 mm fraction and the amount of PCB's in the other two fractions does not exceed ~8-10% of that in the fraction of <0.50 mm. The results obtained from the PCB analysis showed that all of the soil should be treated for PCB's, because the interim remediation criteria sets 50 ppm for PCB concentrations in commercial/industrial site.

A Thin Film Composite (TFC) nanofiltration membrane with a cut off of 150 MW was used to study the feasibility of the solvent recovery and PCB concentration via membranes. A PCB soulution of 2ppm in Hexane was used. The PCB solution was passed through the membrane using Nitrogen gas at 100 psi. Unfortuntely, no rejection was obtained and the membrane test failed.

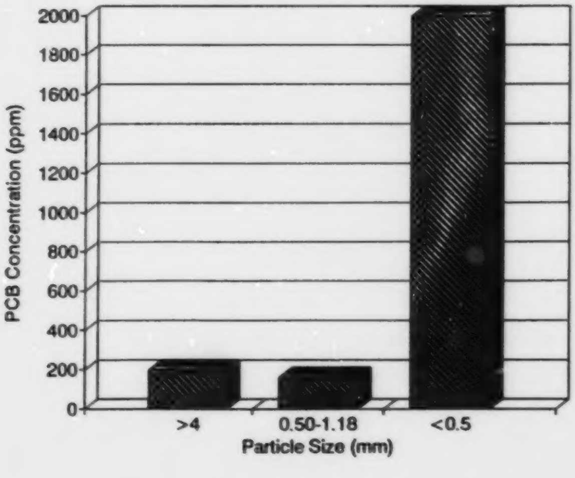

FIGURE 9. Distribution of PCB's in the test soil.

Proposed Process

The following diagram shows the proposed process for removal of heavy metals and PCB's from the contaminated soil:

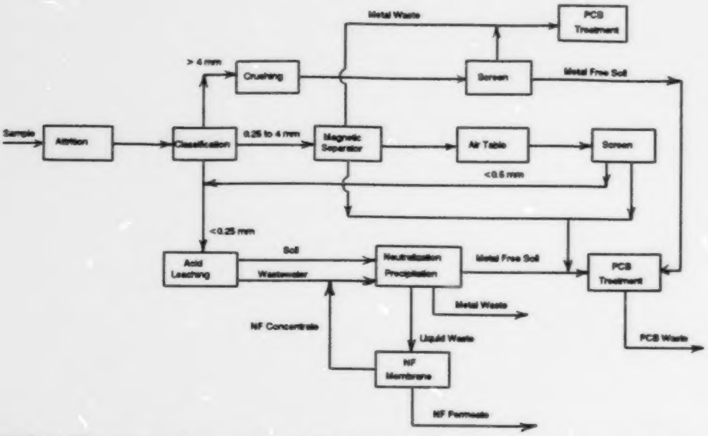
Metal Waste
PCB Treatment
> 4 mm
Crushing
Screen
Metal Free Soil
Sample
Attrition
Classification
0.25 to 4 mm
Magnetic Separator
Air Table
Screen
<0.5 mm
<0.25 mm
Acid Leaching
Soil
Wastewater
Neutralization Precipitation
Metal Free Soil
PCB Treatment
Metal Waste
NF Concentrate
Liquid Waste
PCB Waste
NF Membrane
NF Permeate

FIGURE 10. The proposed process flow sheet for remediation of soil contaminated with heavy metals and PCB's.

As it can be seen in the above process train, there are two PCB removal steps. The PCB removal could be carried out prior to mechanical treatments and the above process train would still be valid. Incorporating the PCB removal step prior to mechanical treatments would change the physical characteristics of the soil, as well as the metal distribution in different fractions due to change in the size of those fractions. The change in the fraction size would lead to a large amount of sludge to be treated for AL.

CONCLUSIONS

1. A process train was developed for the removal of the heavy metals from the contaminated soil. It consists of mechanical, physical and chemical treatment methods.

2. The majority of metals were removed by crushing, screening and the use of an air table.

3. Magnetic separation improved the efficiency of the process by reducing the amount of material that had to be processed.

4. Acid leaching was required to remove the heavy metals from the soil fractions less than 0.50 mm in size. When acid leaching was integrated with the mechanical and physical processes, the separation efficiency was enhanced.

5. Reagent precipitation reduced the concentration of heavy metals by several orders of magnitude.

6. Employing nanofiltration on spiked PCB solvent extraction liquid waste for PCB concentration and solvent regeneration did not work.

7. The potential process train resulting from this project would incorporate the following steps:
   - attrition of raw soil;
   - dry classification;
   - mechanical and physical separation of the metals;
   - acid leaching;
   - treatment of wastewater;
   - removal of PCB's.

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REMOVAL OF VOLATILE ORGANIC CONTAMINANTS FROM A MUNICIPAL WATER WELL SUPPLY BY AIR STRIPPING
A CASE STUDY: FERGUS, ONTARIO

by
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BACKGROUND

The town of Fergus is located in Wellington County, Ontario. Figure 1 locates Fergus within the province. Fergus has a population of approximately 6800 people.

Fergus' water supply is provided by five municipal wells which in total produce up to 5 m^3/min (1100 IGPM) of groundwater from the limestone Amabel Aquifer system. Trichloroethylene (TCE) was detected in the water supplied from Municipal Well #1 (MW1) at levels up to 80 parts per billion (ppb) in September of 1989. MW1 supplies approximately 1.1 m^3 (250 IGPM) or 22% of the town water supply and was immediately taken off line. The well could not be permanently taken off line due to supply concerns regarding peak water usage, and fire flow requirements, in the upcoming summer season.

Fergus considered it was imperative to bring MW1 back on line as soon as possible, and retained Comcor Waste Systems Ltd. (Comcor) to review treatment levels and treatment system options for TCE removal in the water supplied by MW1. A preferred treatment system was to be selected, designed and installed.

APPLICABLE TREATMENT STANDARDS AND LEVELS OF RISK

The Ministry of the Environment (MOE) for the province Ontario had no approved drinking water standard for TCE in late 1989. A treatment standard for TCE had to be selected before a preferred technology could be chosen. Drinking water standards for TCE as published by various agencies were viewed. Table 1 presents the levels reviewed with the associated level of risk of causing death by cancer through the ingestion of TCE contaminated water over a life time.

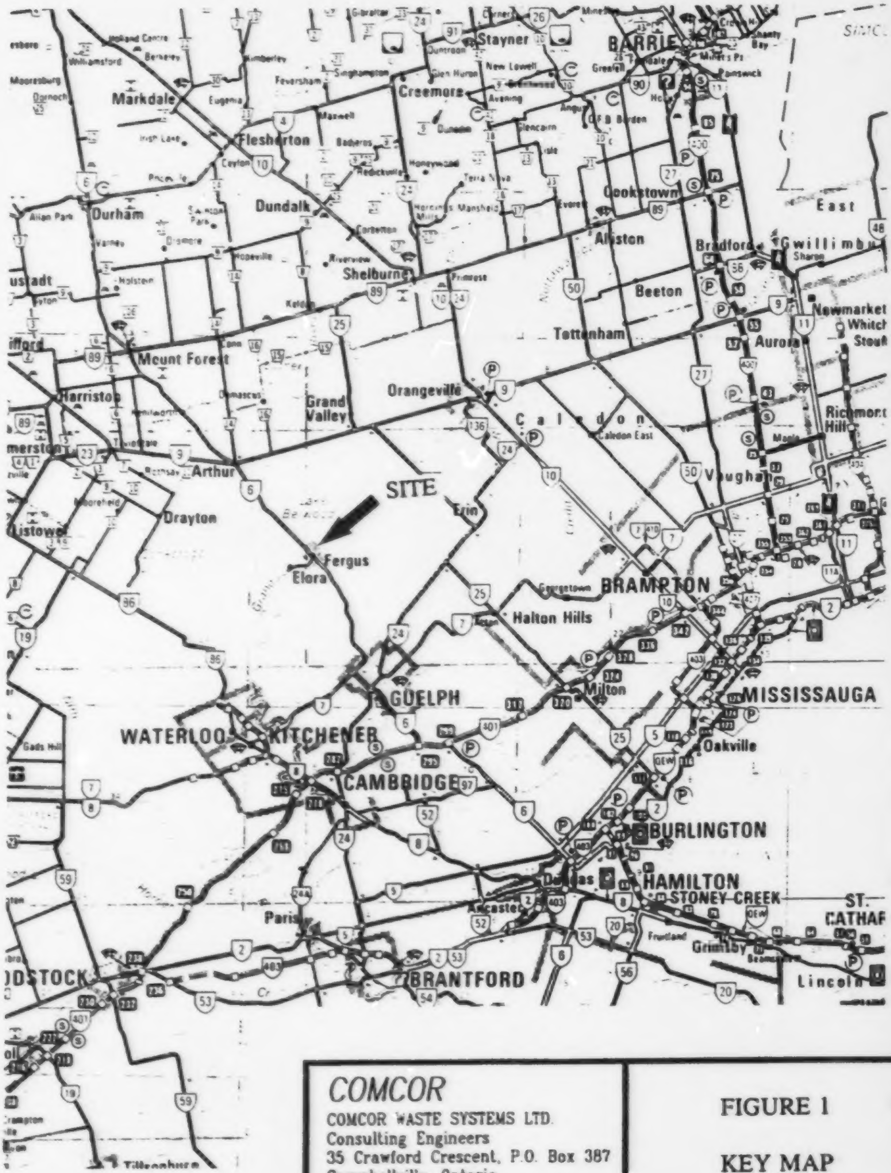
SITE
Fergus
Elora
Erin
Arthur
Drayton
Listowel
Harriston
Mount Forest
Grand Valley
Orangeville
Caledon
Shelburne
Dundalk
Flesherton
Markdale
Durham
Creemore
Stayner
BARRIE
Cookstown
Alliston
Beeton
Tottenham
Bradford
Newmarket
Aurora
Richmond Hill
Vaughan
BRAMPTON
Halton Hills
Milton
MISSISSAUGA
Oakville
BURLINGTON
HAMILTON
STONEY CREEK
Dundas
Ancaster
Grimsby
Lincoln
ST. CATHARINES
GUELPH
WATERLOO
KITCHENER
CAMBRIDGE
Paris
BRANTFORD
WOODSTOCK
Tillsonburg

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FIGURE 1

KEY MAP

Table 1

AGENCY GUIDELINES FOR TCE IN DRINKING WATER

Agency	Maximum Acceptable Concentration	Approximate Risk Level *
WHO	30	1:100,000
U.S. EPA	5	1:1,000,000.0

* Risk level based on consumption of 1.5l of water per day by a 70 kg. person for 70 years.

A risk level of 1:1,000,000 was considered to be appropriate and, therefore, a treatment level of 3 ppb, based on World Health Organization (WHO) standards was selected. Since this time the MOE has proposed a draft maximum acceptable concentration for TCE in drinking water of 5 ppb.

The 1 in a million risk was considered appropriate as it equates with everyday risks as listed on Table 2. For example the 1 in a million risk is equivalent to the risk of dying from cancer caused by radiation from one chest x-ray over a lifetime. The community as a whole might expect 1 additional cancer occurrence above normal over the next 11,550 years, given the current population, and a 3 ppb level of TCE in the drinking water.

TREATMENT TECHNOLOGY SELECTION

Three (3) treatment technologies were reviewed in order to select a preferred technology for treatment of water supplied from MW1. The 3 technologies reviewed included (1) Air Stripping (2) Activated Carbon Adsorption (3) Oxidation Technologies (U.V. oxidation). A summary of the factors considered when reviewing the alternatives is included in Table 3.

An air stripper was chosen as the best water treatment technology for the Town of Fergus. Air stripping for TCE was considered to be well proven, simple to operate and maintain. The air stripper was by far the least costly treatment system, and could be designed and installed in a relatively short time period.

TREATMENT SYSTEM DESIGN AND PILOT TESTING

A pilot scale treatment test was conducted on-site by Comcor using water pumped directly from MW1. This test was undertaken to determine mass transfer coefficients for TCE from the pumped water to air for system design. Various combinations of water flow and air flow rates were utilized to determine the most appropriate mass transfer coefficients. The mass transfer coefficient allows critical variables, such as packing depth, to be calculated.

Table 2

Risks Which Increase the Chance of Death By 1 In One Million

ACTIVITY	CAUSE OF DEATH
Smoking 1.4 cigarettes	Cancer, heart disease
Drinking 1/2 litre of wine	Cirrhosis of the liver
Living 2 days in New York of Boston	Air pollution
Living 2 months in Denver on vacation from NY	Cancer caused by cosmic radiation
Living 2 months in average stone or brick bldg.	Cancer caused by natural radioactivity
Travelling 6 minutes by canoe	Accident
Travelling 10 miles by bicycle	Accident
Travelling 300 miles by car	Accident
Flying 1000 miles by jet	Accident
Flying 8000 miles by jet	Cancer caused by cosmic radiation
One chest x-ray	Cancer caused by radiation
Eating 40 tablespoons of peanut butter	Liver cancer caused by aflatoxin B
Drinking Miami drinking water for 1 year	Cancer caused by chloroform
Drinking 30 12-oz cans of diet soda	Cancer caused by saccharin
Eating 100 charcoal-broiled steaks	Cancer from benzopyrene

Source: Richard Wilson, "Analyzing the Daily Risks of Life, "Technology Review, February 1979, p. 45.

Table 3

SELECTION CRITERIA

FACTOR	AIR STRIPPER	GAC FILTRATION	OXIDATION TECHNOLOGIES
Ability to Meet 3 ppb treatment criteria	YES	YES	YES
Treatment Cost $ / 1000 gals (including amortized capital costs)	0.10	1.10	$2.00- $3.00
Initial Capital Costs	$40,000	$300,000	$400,000
Proven Technology	Well Proven	Well Proven	Emerging/Proven
Timing (in place for summer peaks)	YES	NO	NO
Waste Emissions	YES (Air)	YES (Solid and/or Air)	NO
Potential By-Products In Water Stream	NO	NO	YES
Ease of Operation	Simple	Simple	More Complex

The analysis of test results on treatment efficiencies indicated a water to air ratio (volume:volume) of 100:1, a mass transfer coefficient of 0.00625 sec^{-1} and a liquid loading rate of 0.011 m^3/m^2 sec as most appropriate for the system design to ensure treatment to levels of 3 ppb or lower. Figure 2 presents a graph of the test results. Based on these three design parameters, an air stripper of 1.52 metre diameter, 8.0 metre depth of #2 TRIPAC packing material, 1890 l/sec (4000 CFM) of air flow, and a design water flow of 16.9 l/sec (250 IGPM) was designed to ensure treatment of MW1 water to a TCE level of 3 ppb or less.

AIR STRIPPER OPERATION AND APPROVALS

MOE Ontario Water Resources Sec.23 approvals, and Environmental Protection Act Section 8 approvals for air emissions were obtained prior to operation of the system. Maximum air emission levels of 590 $\mu g/m^3$ of TCE in discharge air have been calculated. This level is 47 times below current MOE ambient air quality criteria of 28,000 $\mu g/m^3$ and 457 times lower than current American Conference of Government Industrial Hygienists work place time weighted average level of 270,000 $\mu g/m^3$. Further, TCE has a half life of 8 hours in the atmosphere, further reducing the air emission significance.

The air stripper was manufactured by Fabricated Plastics Company of Mississauga, and was installed by Town of Fergus Public Utilities Commission staff in the summer of 1990. The air stripper was constructed of fiberglass under applicable CO-SB41-GP-22 standards.

The air stripper has been in full time operation since September 1990. Water samples collected from the air stripper, and analyzed, have consistently shown results of less than 1 ppb. This is far below the design treatment goal. Before and after chemical analysis of the treated water is provided in Table 4.

There have been no operational difficulties to date with the system. Inorganic precipitates are likely forming on the packing material. Pre and post treatment

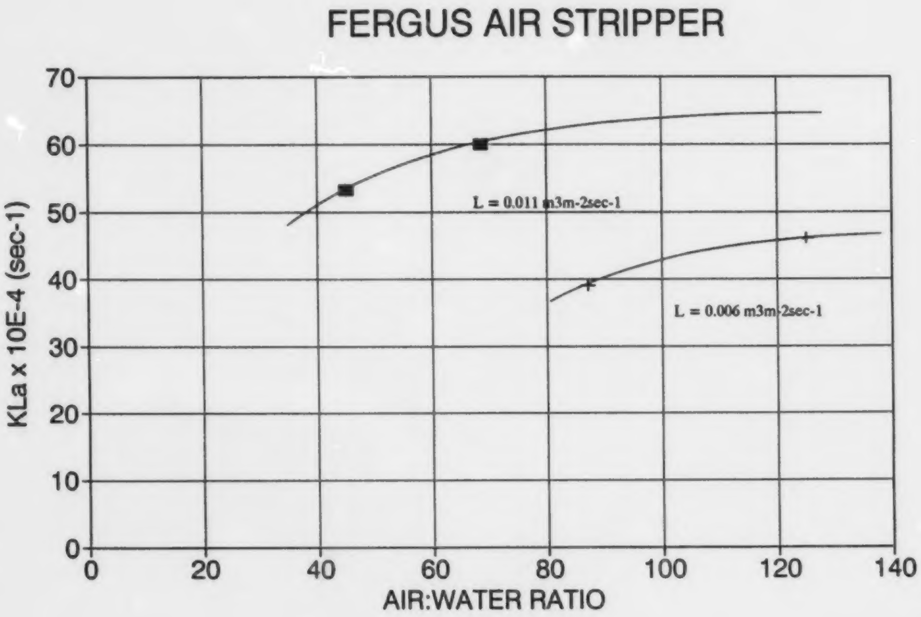

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FIGURE 2

PILOT TEST RESULTS

Table 4

Water Treatment Chemical Analysis

PARAMETER	INFLUENT	EFFLUENT	DRINKING WATER STANDARD	METHOD DETECTION LIMIT
TCE	77.7	ND		1.0 ug/L
Sodium	42.0	42.0	20.0	0.5 mg/L
Potassium	3.2	3.3	----	0.1 mg/L
Calcium	133	106	200	0.005 mg/L
Magnesium	40.0	40.0	150	0.001 mg/L
Hardness ($CaCo_3$)	496	429	___	0.05 mg/L
Alkalinity ($CaCo_3$)	279	257	500	1.0 mg/L
Carbonate ($CaCo_3$)	3.26	3.7	___	1.0 mg/L
Bicarbonate ($CaCo_3$)	276	253	___	1.0 mg/L
Sulphate	194	186	500	1.0 mg/L
Chloride	63.0	63.0	250	1.0 mg/L
Silica (SiO2)	8.6	8.5	___	0.5 mg/L
Ortho Phosphate (P)	< 0.01	< 0.01	0.20	0.01 mg/L
Nitrate + Nitrite (N)	1.30	1.20	10.0	0.05 mg/L
Ammonia (N)	< 0.05	< 0.05	0.50	0.05 mg/L
Colour (true)	< 3.0	4.0	5.0	3.0 TCU
Turbidity	< 0.3	< 0.3	1.0	0.3 NTU
Conductivity (25C)	1250	1080	___	0.1 umho/cm
pH	8.1	8.2	___	0.0 units
Total organic carbon	2.4	1.2	5.0	1.0 mg/L
Iron (total)	< 0.02	< 0.02	0.30	0.02 mg/L
Copper (total)	< 0.01	< 0.01	1.00	0.02 mg/L
Manganese (total)	< 0.01	< 0.01	0.05	0.01 mg/L
Zinc (total)	0.09	0.07	5.00	0.01 mg/L

ND - non detect

water analysis as shown in Table 4 indicate hardness (as $CaC0_3$) reductions on the order of 10%. This is a relatively minor precipitation rate. The packing was checked in the fall of '91, and the summer of '92 and shows some precipitate formation. This precipitate formation was anticipated, and packing replacement every 3 or 4 years was included in the cost assessment of the treatment system. At the current rate of precipitation the actual time for packing replacement may be longer. No biological fouling of the packing has been noted to date, and is not anticipated to be a problem.

AIR EMISSIONS FROM AIR STRIPPING COLUMNS

Despite their simplicity, ease of operation, low cost and overall elegance of design for water treatment of VOC's, air strippers have increasingly been criticized for their air emissions. Air strippers are often not utilized in appropriate circumstances as it is commonly believed that the US EPA requires off gas treatment on all air strippers regardless of levels of emissions.

There are many states which have no requirements for off gas treatments. The most stringent state, California (Los Angeles Basin) has a de minimus level of 1 lb/dy of total organics before off gas treatment is required. This is equivalent to non-methane organic gas emissions from 20 automobiles running on gasoline or 8 vehicles running on natural gas over 1 year. The Fergus air stripper air emission is equivalent to adding 4 more cars in the town. This would suggest that air emissions from the Fergus air stripper are insignificant and treatment of water streams with TCE contamination in the part per billion level are not of concern with air strippers.

For treatment of water streams with TCE contamination in the parts per million range off gas treatment may be of more significance and may require off gas treatment. Off gas treatment for air strippers has typically involved vapour phase carbon adsorption, incineration, or catalytic oxidation. All these types of emission control system are readily manufactured in the United States. Typically, costs for air stripping with off gas treatment can approach the costs of treatment with granular activated carbon depending on the size of systems required, the volumes of water to be treated and the mass of contaminant to be removed. Therefore, a thorough analysis should be undertaken to determine if air stripping with off gas treatment is the most economically viable system.

ACKNOWLEDGEMENTS

Comcor Waste Systems Limited would like to acknowledge the following individuals who were highly involved in completing this successful project.

Mr. Al McGregor, Superintendent, Fergus Public Utilities Commission
Mr. Dale Murray, P.Eng., Triton Engineering
Mr. Ray Blackport, Terraqua Investigation Ltd.

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THE BLEVE EXPLODED: An Anatomy of a Boiling Liquid Expanding Vapour Explosion

by

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ABSTRACT

The loss of containment (LOC) for Pressure Liquefied Gas (PLG) vessels under accidental fire engulfment or mechanical failure is shown to be very complex. The LOC depends upon: (i) the extent and intensity of external heating, (ii) the pressure relief device (PRD) operation and flare (if contents flammable), (iii) the fluid and fill level, (iv) the type and size of mechanical failure, (v) the construction of the vessel, and (vi) the thermohydraulic history of the commodity prior to failure.

The simple "Pop-Can" experiment described here shows that there exists a new type of more powerful failure than the BLEVE. This event we call a BLCBE, a boiling liquid compressed bubble explosion. A hypothesis is advanced to explain this mode of failure which is supported by an initial series of small scale experiments involving Argon, water, R11, and R123.

A comprehensive set of test programs to determine the details of the BLCBE and BLEVE failure modes is indicated along with work to determine methods of protection.

1. INTRODUCTION AND BACKGROUND

It is proposed that there are three basic types of vessel failure and consequences for pressure liquefied vessels under fire attack. All types of events are initiated by the thermal stratification of the liquid and vapour spaces under sustained heating and the increase in vapour wall metal temperatures [1 - 5]. The pressure relief device (PRD) will activate when the liquid surface temperature and thus its saturation pressure exceeds the PRD opening set point. The type of tank geometry influences, for similar fire exposure and volume, the time to first vent [6] (Figure 1). The valve may cycle or ultimately remain open with contents exiting as appropriate to the pressure and internal flow conditions [4]. The ullage volume wall temperatures lead ultimately to creep rupture in this space with the size of the crack formed plastically dependent upon the available energy in the vapour space alone [7]. The crack will usually form in the hot metal at a position where the PRD flare exposes the metal surface to higher thermal loads [8, 9].

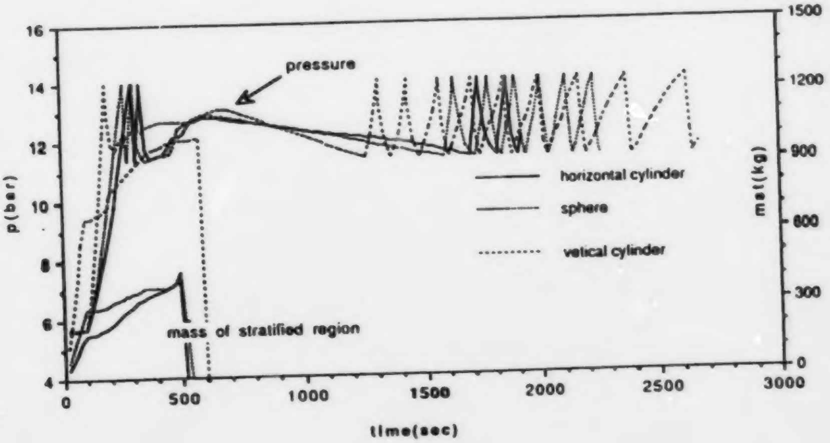

Figure 1. Pressure and stratified liquid mass time development for horizontal and vertical cylinders as well as spheres containing 2 tonnes of propane at 70% volume fill exposed to a totally engulfing pool fire [6].

Dependent upon fill level then, the crack size may be limited to the hot metal regions of the vapour space for large fills or, if over a critical crack size, to regions at or below the liquid level for lower level fills. In this latter case, vessel containment can be totally lost since crack(s) now propagate elastically without restraint and small energy requirements [10a]. An adiabatic expansion of the contents next occurs within limits bounded by either an isenthalpic or an isentropic flash evaporation. For propane under normal storage conditions this results in a 40 to 50 percent flash vapour fraction with the evaporating residue distributed as large droplets or left in the form of a pool [11].

This type of failure has sometimes been called a BLEVE and invariably occurs below some critical fill level when there is sufficient energy in the vapour to cause the crack to propagate plastically to cold metal at or below the liquid level. The event leads to, if the contents are flammable, massive fireballs and residual pool fires. It is not the most violent type of event which can however, occur as little or no blast effect results [11].

More dangerous events can occur, with higher fill levels. In these circumstances the creep rupture crack is arrested in the hot vapour space metal by plastic tip blunting [10b], since there is insufficient available work in the vapour. Then, dependent upon the thermohydraulic history of the liquid, either a massive and prolonged two phase jet discharge will occur, or a catastrophic and very powerful vessel failure with complete loss of containment by a homogeneously nucleated highly compressed two-phase mixture results.

The first type of failure will result with the contents stratified and pressurizing [4] and involves therefore a distribution of non nucleated superheated liquid upon depressurization. The event commences with the discharge of superheated vapour through the narrow creep rupture formed crack, followed, some time after (~ 45 ms) with a heterogeneous wall, nucleated, high void-fraction two-phase discharge of long duration for the scale of experiments described here. A sustained jet or torch fire issuing from the crack may thus follow if the contents are flammable.

The last type of failure occurs with the contents usually homogenous in temperature and depressurizing. It may also be initiated by a sudden release of pressure caused by PRD action and size, the carry over of bubble nuclei into the vessel due to filling operations, or even a leak before break somewhere else in the vessel or its associated plumbing. Like the former failure, a crack is formed in the vapour space and the superheated vapour first discharges. Since the liquid contents now are, however, already nucleated, (due to the falling pressure prior to this crack formation), there is an almost instantaneous (~100 μs) generation of void causing a rapid two-phase swell. This low void-fraction swelled material chokes in the crack and results in a rapid (~40 μs) repressurization of the contents back approximately to the original containment pressure. Collapse (~30 μs) of the vapour bubbles generated by the initial liquid depressurization wave thus occurs. The liquid shock pressures developed by bubble collapse (1-3 kbar) result in the rapid (~ speed of sound in the metal [10c]) elastic crack propagation of the now cooled vapour walls. This LOC occurs extremely rapidly (~ 600 μs) and results in an extremely powerful (~ 20 MW) release.

The highly compressed two-phase material is now suddenly depressurized again. The expansion of the high pressure vapour bubbles, internal to and uniformly distributed throughout the liquid, rapidly shatters and projects the superheated liquid into a fine highly turbulent aerosol. This situation results in the violent, rapid and uniform dispersal of the contents which totally evaporates over a time scale of several tens of milliseconds. The combination of a flammable commodity and power of the event may, under proper conditions, cause an escalation of the incident into a detonation.

Obviously as the temperature of the liquid contents approaches the superheat limit [12] greater numbers of smaller sized bubbles are formed more rapidly, resulting in greater liquid shock pressures upon collapse and thus significantly more powerful events. This type of dual step loss of containment can more properly be called a "Boiling Liquid Compressed Bubble Explosion", or "BLCBE" rather than a BLEVE. It is our view that, based upon the evidence from the incident at Mexico City in 1984, all three types of events were experienced by the spherical LPG storage tanks with tragic consequences [15]. The potential for similar circumstances may also exist in other processing, storage and transportation pressure vessels containing many pressure liquefied fluids. The mechanical failure of vessels, perhaps by crack initiation through shock damage, or other mechanisms can also yield similar type events.

2. PRELIMINARY EXPERIMENTS

Some experimental evidence of the above hypotheses has been obtained using a simple "POP CAN" BLEVE facility [15]. The preliminary results illustrate the BLCBE, BLEVE and other failure behaviour by measurements of the dynamic pressure developed in partially filled vessels, failing under torch fire attack or with mechanical (knife) crack initiations. The experiments, and their high speed (5000-6000 frames/s) photography, permits the rapid, reproducible evaluation of the influence of all variables that may affect the problems and their solution.

2.1 Test Facility and Instrumentation

Aluminum and steel pop cans are used as the testing vessels. Samples of these cans have been tested and shown to fail under hydrostatic pressures of between 130 psig for aluminum and 350 psig for steel. The failures are consistent with tensile tests of the wall materials.

The preremoved tab end of the can is replaced by a fabricated end piece that seals the vessel with a clamp and an "O" ring. This end contains two type T thermocouples in the vapour and liquid spaces, and a dynamic as well as a static pressure transducers. The tank vapour space can be vented to the outside through the fill line. The end piece is rigidly fastened to a blast shield to immobilize the apparatus and protect the instrumentation (Figures 2 and 3).

Dynamic instrumentation consists of a PCB 101A02, 1 μs rise time, (400 k Hz Natural frequency) low impedance quartz pressure transducer with an associated 482A signal conditioner. This unit is coupled to two HP54501A 100 MHz oscilloscopes capable of 20 Mega samples/s at 5 μs/division which under software control can sample 1000 samples/screen. Each oscilloscope is set for specific time range.

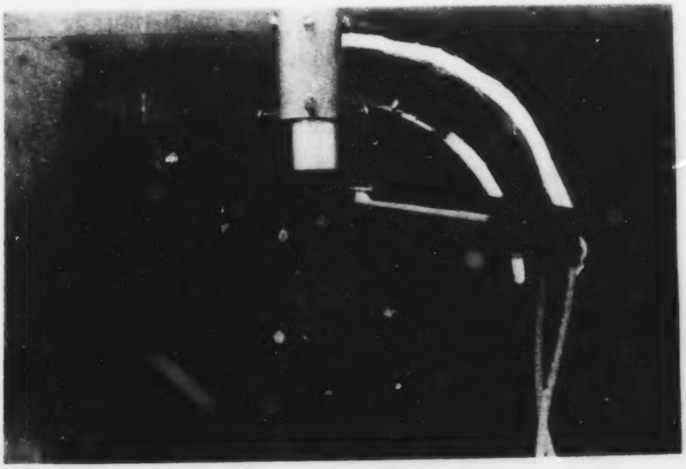

Figure 2: Photograph of "Pop-Can" BLEVE Facility.

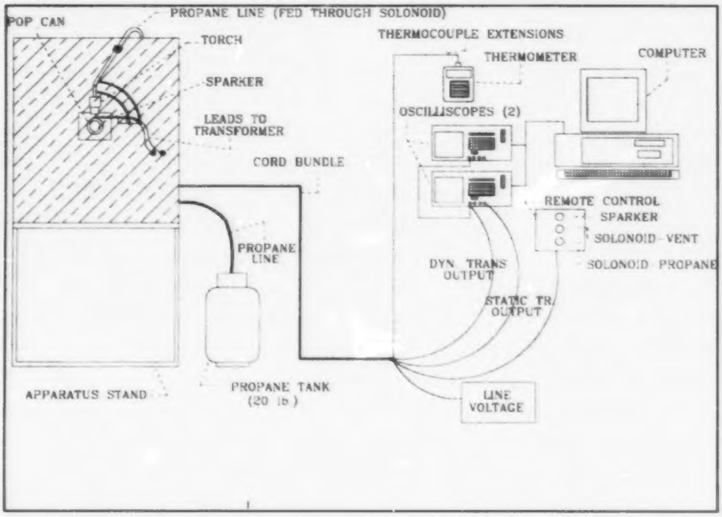
POP CAN
PROPANE LINE (FED THROUGH SOLONOID)
TORCH
SPARKER
LEADS TO TRANSFORMER
CORD BUNDLE
PROPANE LINE
APPARATUS STAND
PROPANE TANK (20 lb)
THERMOCOUPLE EXTENSIONS
THERMOMETER
COMPUTER
OSCILLISCOPES (2)
REMOTE CONTROL
SPARKER
SOLONOID-VENT
SOLONOID PROPANE
DYN. TRANS OUTPUT
STATIC TR. OUTPUT
LINE VOLTAGE

Figure 4: Schematic Diagram of the "Pop-Can" BLEVE Facility and Instrumentation.

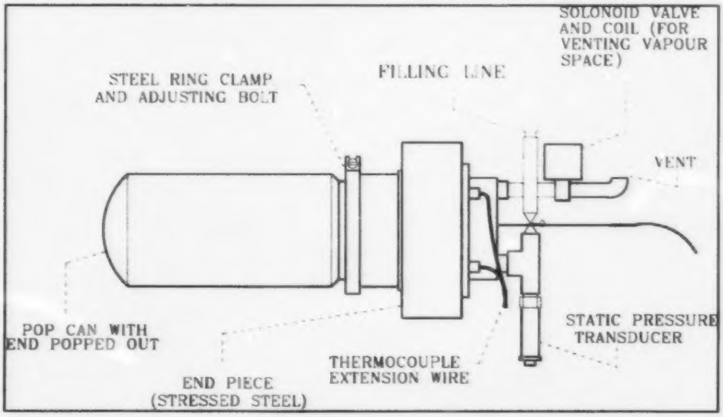
SOLONOID VALVE AND COIL (FOR VENTING VAPOUR SPACE)
STEEL RING CLAMP AND ADJUSTING BOLT
FILLING LINE
VENT
POP CAN WITH END POPPED OUT
STATIC PRESSURE TRANSDUCER
THERMOCOUPLE EXTENSION WIRE
END PIECE (STRESSED STEEL)

Figure 3: Schematic Diagram of the "Pop-Can" BLEVE Facility.

Photography is by a Fastax 16 mm 5000 fps camera. A layout of the experimental facility is shown in Figure 4. Details the instrumentation is give in Appendix 1.

2.2 Some Preliminary Results[1]

Four types of tests have thus far been conducted. Cans with fills of Argon plus Water, Argon only, R 11 and R 123 were failed at 790 kPa (~100 psig). Pressure was maintained either by the gas or by the vapour pressure obtained using a "STERNO" external heater impinging on the liquid space. Failures were initiated by localized vapour space heating using a propane torch Additional failures using a solenoid actuated knife to form preselected crack sizes were also conducted with R22. Pressure signals obtained from an Argon filled and R11 filled test are shown in Figure 5 and 6 respectively. More than fifty experiments have been conducted so far in an attempt to illustrate the complete range of failure behaviour and consequences.

The argon tests were pressurized to 100 psig and the cracks initiated in the horizontal vessel using the propane torch directed on the top central region of the can. The size and intensity of the torch influences the heated region. The size of the initial crack formed is influenced by the available energy in the vapour space, the severity of external liquid space heating, the metal temperature and time. For all the results shown here the torch and external fire temperature settings were maintained constant.

In the Argon tests the tank is plastically destroyed over a millisecond time frame (Figure 5) as the available work in the gas is sufficient to permit crack extension by tearing to complete failure [17,18]. The failure surfaces, shown in the SEM photographs Figures 7 and 8, indicate clearly the plastic deformation resulting.

In the R11 test shown in Figure 6, the original liquid fill was set at 70% by volume. The can was pressurized to 110 psig (Tsat ~ 97°C) using the external "STERNO" heating. The liquid fill is now ~ 80%. The vessel was then quickly vented in the vapour space by a single short vent down to 105 psig. A crack was then initiated in the vapour space wall by the propane torch. This crack arrested when it had developed to one centimeter in length and exhausted the available work of the vapour. The tank was then catastrophically and rapidly (~200 μs) destroyed resulting in the pieces shown in Figure 9. The contents were violently dispersed as a fine and rapidly evaporating aerosol. For R11 the superheat limit T_{SL} is 422 K (149°C) [12] and thus this test is > 50°C below T_{SL}. Peak impulsive sound level intensity at 2.5 m measured end on to the can registered 132 dB for R123.

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[1] An accompanying video of four selected tests should be reviewed prior to examining this section.

The dynamic pressure transducer, located below the liquid surface at the centre of the instrumentation boss indicates that after a preliminary stage of depresurization (~200 μs), caused by the formation and arrest of the initial crack, there is a measured over-pressure of 175 kPa (~25 psig) greater than the original containment. The time rate of increase of this latter pressure rise suggests the development of coherent liquid shock pressure waves caused by bubble collapse [19-21].

An experiment similar to that shown in Figure 6 was conducted without, however, the initial vapour vent prior to failure and thus without prior bulk nucleation. In this test the tank remained intact with the contents discharged as a long duration, approximately one second high void-fraction jet through a 1 cm long initial crack. The edges of the opening became somewhat plastically deformed so that the width is about 2 to 3 mm with a slight (1-3 mm) extension in the length of the crack.

Similar tests to those above were conducted with 70% volumetric fills of unheated water with 100 psig argon gas ballasts. Similar sizes of failure (~1 cm) without, however, the plastic edge deformation resulted in a ~0.1 mm wide cracks.

In two of the above tests the vessel was destroyed. The second event described clearly illustrates a significant pressure rise above the original containment level and sizeable blast effects. This can only be described as a BLCBE.

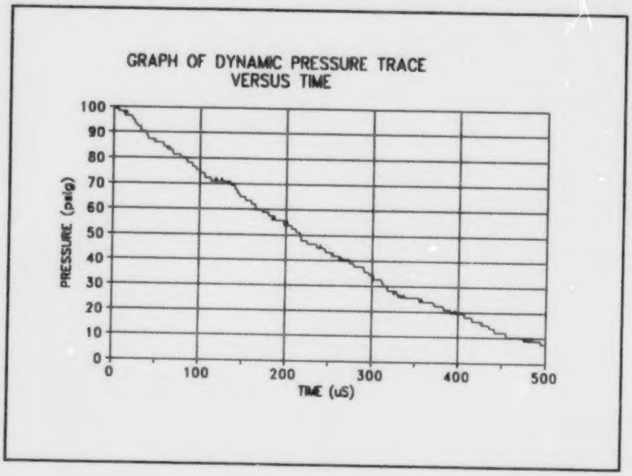

Figure 5: Dynamic Pressure Trace of Argon Filled Vessel, at 790 kPa (100 psig) and 25°C, torch failed.

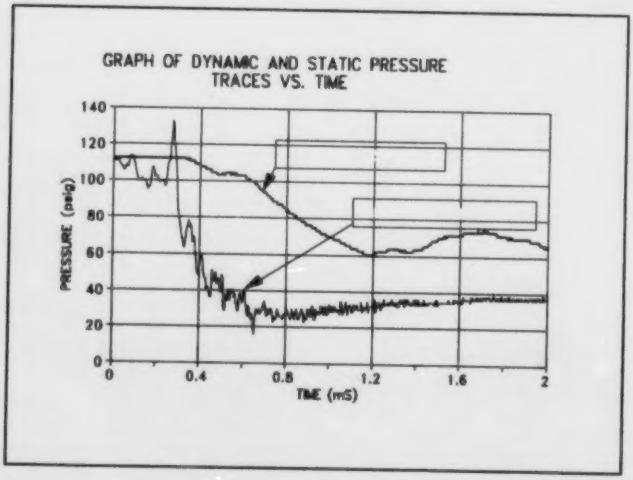

Figure 6(a): Dynamic and Static Pressure Traces; Test# 5, 70% (Vol.) R 11 Initial Fill, Externally Heated to 860 kPa (110 psig) and torch failed.

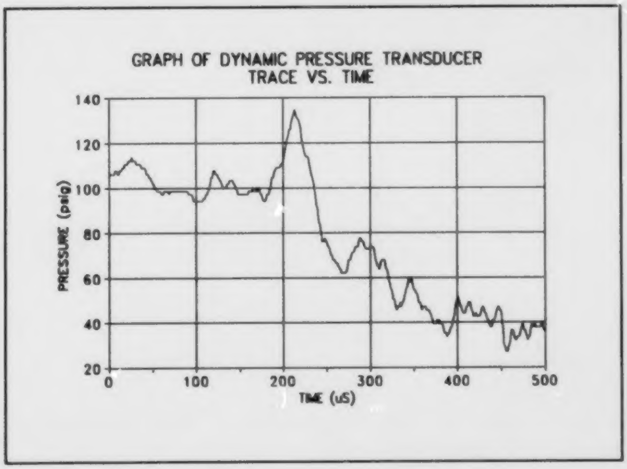

Figure 6(b): Expanded Time Scale of Dynamic Pressure Trace, Test# 5 as of Figure 6(a).

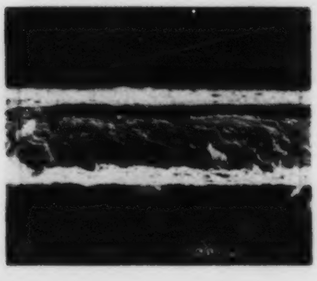

Figure 7(a): SEM Plastic Fracture Surface, Argon Vessel (Magnification x 300).

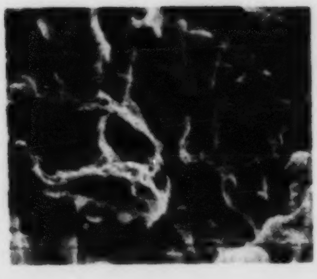

Figure 7(b): SEM Plastic Fracture Surface, Argon Vessel (Magnification x 5000).

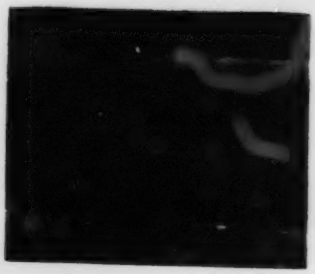

Figure 8(a): SEM Elastic Fracture Surface, Test# 5, R 11 (Magnification x 500).

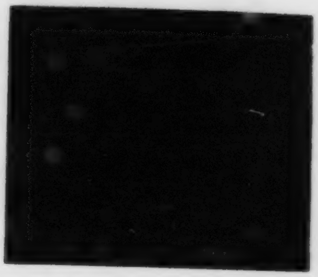

Figure 8(b): SEM Elastic Fracture Surface, Argon Vessel (Magnification x 5000).

Figure 9: Vessel destruction BLCBE Failure (Test 5)

3. DISCUSSION

The observed modes of failure in the described tests ranged from, (i) the formation of arrested cracks in the vapour space, for the water and non nucleated R11 fills, (ii) the complete tearing apart of the vessel by gas pressure, to, (iii) the very powerful events with prenucleated partial fills of R11 and R123.

Up to now the BLEVE phenomenon has been portrayed as a single step event [11, 12, 15, 22-24] which is initiated by the LOC and results in the adiabatic flash evaporation and dispersal of the contents. Obviously from the test data presented here there is, additionally, the possibility of much more powerful incidents with higher fills. This, the BLCBE, requires prior nucleation of the liquid contents, and may occur very early on in the accident. This failure is a two stage event leading to the violent, rapid dispersal of the total contents as a small sized evaporating aerosol with significant blast over-pressures.

It is hypothesized that the liquid shock pressures generated by vapour bubble collapse are responsible for the rapid destruction of the containment vessel and the dispersal of the contents as the aerosol. The evidence for this statement is based upon many small scale fully instrumented trials such as described above.

In the events which BLCBE'd the average peak over-pressures recorded, relative to either an argon depressurization trace, for the same containment pressure, or an envelope developed by the minimum pressures in the recorded trace, were 490 kPa (70 psig) in a sample size of 10 trials (min 380 (55 psig), max 590 kPa (85 psig)). On the basis that the pressure wave commences at the centre of the original 1 cm long crack, the instantaneous over-pressure exerted at the crack tip is 6.2 MPa (62 bar or 900 psig)! Crack reinitiations at such large rates of strain (1.6 x 10^5 MPa/s) can result in elastic propagation velocities approaching a significant fraction of the speed of sound in the metal. The mechanical energy required to recommence crack propagation at such velocities though in general derives from the thermal energy of the contents it is small (<1%) and once started crack propagation requires little further energy [10b].

A bubble collapse time derived by taking one half the peak overpressure base time pedestal of ~80 μs (Figure 6) yields bubble sizes for inertial collapse in the range for 1 to 3 mm diameter [19,20]. Bubbles of this size are also generated at atmospheric pressure inertially and thermally, in the 100-200 μs time delay times observed [12]. Since containment is lost so rapidly (~ 600 μs) the adiabatic flash of its contents and the commencement of inertial fragmentation and dispersal of the contents is extremely powerful (> 20 MW).

The formation and observed evaporation of the aerosol from the total contents can also be inferred by the proposed BLCBE mechanism. Although the models are crude they can serve to indicate areas necessary for further experiments and more refined models.

The high speed photographic evidence indicates that after the initial vapour discharge of some 8-12 ms, no further fluid leaves the tank prior to its ultimate failure. If the proposed hypothesis is correct therefore, the tank at this time must be uniformly full of a low void fraction two-phase mixture whose bubbles are ~ 1-3 mm in diameter. The approximate number of bubbles can therefore be estimated from the vapour volume existing at the time of the initial creep rupture. As the bubbles are presumed to be uniformly distributed throughout the fluid, a liquid volume associated with each bubble can be determined for which a Weber number formed using the kinetic energy of the bubble and the liquid surface tension can be estimated. Inertial bubble expansion velocities [12] and the volumes of associated liquid yield such values such to suggest an aerosol formed of ~200 μm diameter droplets. Such an aerosol is observed to rapidly (~ 40 - 60 ms) evaporate. If flammable, a fire ball will result upon ignition and may, under appropriate conditions, detonate since the powerful initiating LOC could act as a trigger.

4. CONCLUSIONS

A simple "Pop-Can" BLEVE experiment has revealed the existence of a loss of containment event called a Boiling Liquid Compressed Bubble Explosion, a "BLCBE". Such an event is more powerful than the BLEVE and is at an extremum of failure types that range from it to the BLEVE and ultimately down to those which result only in the expulsion of their contents as a flashing two-phase jet. All the events and their interrelationships are obviously very complex and have many interacting dynamic components. Obviously, as the contents of such vessels approach the superheat limit [12] even more powerful events are possible.

The generic features of the BLCBE consist of:

(i) partial failure either mechanically or thermally of the containment vessel.

(ii) multiple bubble initiation, and growth in a prenucleated bulk liquid.

(iii) rapid two-phase swell, repressurization and coherent collapse of the bubbles formed.

(iv) bubble collapse shock pressure failure of the previously damaged vessel.

(v) violent distribution of the compressed two-phase contents as extremely fine evaporating aerosol with significant blast, and

(vi) if contents are flammable, the potential for a detonation.

The initiation of the bubble nuclei responsible for this type of failure may either be the PRD operation and size, bubble retention in the bulk fluid resulting from filling operations, or even a leak. The selection criteria for PRDs and the "leak before break" philosophy widely utilized in the process and power industries for loss control may therefore deserve more careful scrutiny. The significance of this hypothesis relative to the protection of chemical reactors should also be examined.

5. RECOMMENDATIONS

There is a requirement for definitive experiments to confirm and amplify the sequences of events described here for all types of losses of containment. Such experiments should seek to more fully understand the phenomena such to permit models to be developed of all aspects of the thermohydraulics leading to the failure types described. These experiments should be structured to provide a clear demarcation between the classes of events and the significance of their consequences. This work can best be done in a staged approach that first utilizes small scale experiments to understand the various elements and their complex interactions. Next, verified sub-models of the individual components should be developed and assembled into a comprehensive computer code to be utilized in predicting the outcome of a selected series of larger scale experiments. At this time various proven prevention/mitigation techniques should be examined.

The Part I test program envisaged would provide for (i) a clarification and quantification of the creep rupture and other failure mechanisms (material and fire exposure aspects, time to failure and size of failure(s)) as a function of tank heating as well as volumetric fill and fluid, (ii) the reproducible determination of the initiating event(s) and the subsequent consequences using small scale vessels and high speed pressure as well as photographic ($4 * 10^3$ - $1 * 10^6$ fps) records. These would examine the interrelationships between fluids (flammable and non-flammable), original fill, stratification, restriction geometry, and pre-failure pressure history as well as explosive potential.

These tests should permit the determination of the exact sequence of the events and provide a basis for the examination of several methods of prevention.

The results should, as well, permit verified submodel incorporation into the necessary computer codes that will be of use in the development of protection strategies and for first responders.

The small scale tests should be followed by larger scale fire and other failure type trials (Part II), which must be designed to provide confirmation of the small scale results and illustrate determined preventive measures.

An inter-university and inter-agency proposal for this work is being prepared for consideration by a selection of potential sponsors including inter-governmental agencies and industrial petrochemical and transportation companies.

6. ACKNOWLEDGEMENTS

Discussions with colleagues, too numerous to list, have over the past eight years aided the senior author's preparation of this work. Financial support has been provided by Natural Sciences and Engineering Research Council of Canada, Transport Canada, Environment Canada, and the University of New Brunswick.

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Apppendix 1: INSTRUMENTATION SPECIFICATIONS

(1) Dynamic Pressure Transducer:

Type: PCB piezoelectric medium pressure transducer (#101A02)
Max. pressure: 10 000 psig
Sensitivity: 1.04 mV /psi
Range: 0 to 10 volts
Rise Time: 1 uS
Resonant Frequency: 400 kHz
Discharge Time Constant: 500 seconds
Temperature Range (F): -100 to +275

(2) Static Pressure Transducer:

Type: Ashcroft sealed diaphragm transducer
(#ASH-S-050-5-M02-05-F2-500)
Max. pressure: 500 psig
Range: 0 to 50 Vdc
Temperature Range(°F): -55 to 195

(3) Hewlett Packard 54501A digital oscilloscope:

100 MHz for repeating signal
5 MHz for single event
500 points per screen
HBIP interface board
Adjustable Trigger

(4) Type-T thermocouple

Type: Copper-constantan
Temperature Range: -200 to 350° C
EMF(mV) Range: -5.602 to 17.816
Limits of Error: 0.75% above 0°C

(5) Photography

Fastax camera set at 5000 frames/second (200 μs/frame)

BOILING, EVAPORATION, AND EXTREME COOLING WITHIN A SUPERHEATED LIQUID JET

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Abstract

A simple thermodynamic model provides a good description of several physical processes occurring during the continuous release of a superheated liquid jet. The data suggest that there is a zone of quasi-equilibrium of several metres in length adjacent to the outlet. It can be modelled as if air entrainment occurs instantly at the exit. Air entrainment is found to be proportional to the liquid mass flow and to the flash fraction. After the entrainment, the jet mixture of liquid, vapour, and air rapidly come into equilibrium. Processes which are examined are (1) fluid emission rate, (2) flashing and droplet formation, (3) air entrainment, evaporation, and cooling. Output from the model includes flow temperature and flow rates for liquid emission from tank, liquid fallout to ground, suspended droplets, and vapour. Results are compared to experimental data gathered within 15 m of the jet orifice.

Introduction

Source modelling is a relatively new pursuit in the dispersion modelling community. Dispersion modellers have been challenged for years to improve their descriptions of plume growth rates. More recently, spills of chemicals leading to the generation of dense plumes have complicated the challenge. Now the source of greatest uncertainty in a concentration calculation is not the plume growth rate but the source emission and gas generation rate. The emission may be either a planned or an accidental release of a gas, pressurized liquid, or cryogenic liquid. It may be a single phase or a two phase jet, or an evaporating or boiling liquid pool.

Many chemicals are stored and transported in liquid form rather than vapour form to take advantage of the volume reduction. If the container breaks, it is important to know the chemical emission rate and the physical properties of the flow. The behaviour of pure vapours and non-boiling liquids is relatively well known. The behaviour of a superheated liquid is less well understood.

This paper examines a superheated liquid jet which is single phase prior to emission. The emission occurs from a pressurized vessel receiving a puncture below the liquid level. Some papers on this topic were presented at the International Conference on Vapour Cloud Modelling in Cambridge, Massachusetts in 1987. Emerson [1] presents a three stage box model in which the first stage describes the entry of the liquid into the air. Turbulent entrainment is governed by the commonly used Ricou and Spalding [2] relations. Emerson assumes that a liquid jet entrains in the same way as a vapour jet. The liquid is assumed to break into droplets of uniform size, depending upon discharge velocity and degree of superheat. Drop trajectories determine the degree of and time for rainout. There is little discussion of evaporation or temperature. Few equations are given.

Fauske and Epstein [3] examine a liquid discharge and subsequent flashing, deceleration, evaporation and cooling. They describe the evaporative cooling below the boiling point that may occur if the evaporating chemical tries to maintain its vapour pressure at its saturation value as air is entrained. There is no droplet or rainout sub-model. Some tests by Lantzy et al [4] with superheated liquid jets of monomethylamine provide some qualitative information on droplet characteristics during hydraulic and flash atomization.

Recently, the Centre for Chemical Process Safety (CCPS) of the American Institute of Chemical Engineers has undertaken a multi-year study to clarify the processes associated with chemical releases. This includes both model development and experimental studies. Preliminary results of both were compared recently by Johnson and Deiner [5], with the model showing significant deviations from the measurements. The experimental results are particularly interesting and form the foundation for the model which is developed in the present paper.

Experimental results

Details of the experiments are given in a paper by Johnson and Deiner [5]. The chemicals used are water, freon-11, chlorine, monomethylamine, and cyclohexane. The number of experiments used in this paper for each chemical are 21, 15, 13, 14, and 10 respectively. The controlling parameters are orifice diameter, and container temperature and over-pressure. These govern the release rate $\dot{m}_{\ell 0}$ and flash fraction f_{g1}. Liquid fallout is captured in pans, giving a measure of fractional liquid capture f_c and its temperature T. Ambient wind speed and temperature were measured but do not seem to affect the results.

As the superheated liquid emerges, part of it boils and part of it evaporates. The remainder, if any, falls to the ground where it is collected. Even for no superheat, there is significant loss of liquid by evaporation for four of the chemicals. The liquid fractions collected are plotted against superheat by Johnson and Deiner [5], and against flash fraction in the present paper (Fig. 1). (Model results are also plotted but should be ignored for the present.) The data suggest that there are two competing mechanisms for converting the liquid to vapour. One dominates at low f_{g1} (or superheat), during which the curve is flat. The other dominates at larger superheats, as the curve drops toward zero. Experiments by Lantzy et al [4] show that large droplets are formed by hydraulic atomization at low superheats and fall from the jet. Fine droplets are created at large superheats and remain suspended. Furthermore, the data in Fig. 1 are stratified approximately by their boiling point temperatures, ranging from 236K for chlorine to 372K for water.

Box modelling

Normally, model development proceeds as a series of reasonable hypotheses which serve to explain observations. Occasionally, empirical or heuristic components may serve as adequate or temporary solutions to an otherwise complex or intractable problem. In this paper, we are choosing a box model approach in contrast to a time-dependent three-dimensional analysis of a complex fluid mechanical problem. A box model frequently allows one to extract most of the essential information with relatively little effort. A good box model contains only the dominating physical processes; as such, it may explain very clearly what is happening. A good complex model retains all processes, which may give good answers but which may obscure the understanding.

The liquid passes through the following stages: (1) Bernoulli flow from the container, (2) flashing, and cooling to the boiling point, (3) air entrainment, evaporation, and further cooling. The first two stages are well understood but are included here for continuity. Stage two is rapid and is completed close to the orifice. A fraction of the superheated liquid boils instantly, resulting in a two-phase liquid/gas flow at the boiling point temperature. Stage three seems to have both a fast and a slow temporal response. The fast response is due to the impulsive nature of the fluid emission in disturbing the air, causing rapid entrainment. Equilibration to the impulse is slower and occurs over a distance of a few metres. Concurrently, classical jet entrainment continues even further for several tens of metres as the jet grows and decelerates. The latter process is not discussed in this paper but has been studied extensively (Fauske and Epstein, [6]). These stages are represented separately and in succession by the four zones of Fig. 2.

Bernoulli emission and flashing - Zone 1

Bernoulli's equation is a reasonable starting point for describing the flow rate of the liquid from the pressurized tank. The pressure difference which expels the liquid is P_0-P_∞, where P_0 and P_∞ are the tank and ambient pressures, respectively. The tank pressure in these experiments consists of the equilibrium vapour pressure $P_{eq}(T_0)$ at the tank temperature T_0 plus an imposed overpressure ΔP. An overpressure of several kilopascals serves to regulate the mass flow from the nozzle, and to impart a moderate mass flow when the liquid in the tank is at or below the atmospheric boiling point temperature T_b. The overpressure also serves to prevent or reduce the onset of flashing within or before the exit orifice. The head pressure due to the height of the liquid is always much less than ΔP and can be ignored. Hence the Bernoulli emission flux is described by

$$G_B = C_d(2\rho_\ell(P_0-P_\infty))^{1/2} \qquad (1)$$

where ρ_ℓ is the liquid density, and C_d is the discharge coefficient. The experiment was designed to minimize pressure losses in the pipe leading to the nozzle. When Eqn. (1) was used to predict the mass flows, it underpredicted at low pressures, and overpredicted at high pressures, using the usual value of $C_d=0.61$ for a sharp-edged orifice. Since C_d is an empirical coefficient and is dependent upon several parameters, it may be that another value is more suitable for these orifices.

At higher pressures, created by higher stagnation temperatures, the liquid flashes upon exiting the orifice. If it begins to flash within the orifice, where the pressure gradient is very steep, the downstream pressure upon the pure liquid phase is increased above P_∞, reducing the Bernoulli flow. If the mass flux data are nondimensionalized by G_B and plotted against the flash fraction f_{gl}, the departure below the ideal Bernoulli flow ordinate value of unity is evident (Fig.

3). Although the departure may be due to causes other than flashing, a reasonable fit through the data is provided by an empirical modification to Eqn. (1) given by

$$G = G_B/(1.+f_{g1}) \tag{2}$$

using a discharge coefficient of $C_d = 0.7$. The flash fraction is the ratio of gas mass flow $\dot{m}_{g1}$, produced by the boiling of the emitted superheated liquid, to the original liquid mass flow $\dot{m}_{\ell 0}$. It is expressed as [6]

$$f_{g1} = \dot{m}_{g1}/\dot{m}_{\ell 0} = c_\ell (T_0 - T_b)/h_{\ell g} \tag{3}$$

where c_ℓ is the liquid specific heat, $h_{\ell g}$ is the heat of vaporization, and $\dot{m}_{\ell 0} = GA_0$ (A_0 is the area of the orifice). Subscript 0 refers to stagnation conditions in the tank, and subscript 1 refers to the zone of instantaneous flashing immediately following the orifice (Fig. 2). The liquid flow rate in Zone 1 is given by

$$\dot{m}_{\ell 1} = \dot{m}_{\ell 0} - \dot{m}_{g1}. \tag{4a}$$

or, dividing by $\dot{m}_{\ell 0}$,

$$f_{\ell 1} = 1 - f_{g1} \tag{4b}$$

Rapid air entrainment - Zone 2

During and following the flashing process, air is entrained due to the turbulence created by the impulsive motion and phase change of the jet. These processes can be treated as two successive equilibria: pure boiling (Zone 1) followed by entrainment and evaporation (Zone 2). The flash equation (Eqn. 3) can be derived from an energy balance between Zone 0 and Zone 1. Similarly, conditions in Zone 2 can be related to Zone 1. Zone 1 consists of a mixture of liquid (contiguous and droplet) and vapour at the boiling point temperature. We assume that a finite amount of air is entrained at the beginning of Zone 2. The air adds a minute amount of warmth to the mixture. The overwhelming effect is to add volume which lowers the partial pressure of the vapour. This causes some liquid to evaporate until an equilibrium is established among the air and chemical species and the vapour and liquid phases. Equilibrium implies that vapour and liquid phases are saturated.

In the thermodynamics of flow processes, one can define a control volume which encompasses the boundary region of Zones 1 and 2. The energy which flows into the control volume from Zone 1 must equal the energy which flows out of the volume in Zone 2. Pressure work and kinetic energy changes are relatively small and can be ignored. An enthalpy balance between Zones 1 and 2 for all the participating mass flows allows us to write

$$\dot{m}_{\ell 1} h_{\ell 1} + \dot{m}_{g1} h_{g1} + \dot{m}_{a\infty} h_{a\infty} = \dot{m}_\ell h_\ell + \dot{m}_g h_g + \dot{m}_a h_a \tag{5}$$

where subscripts ℓ,g,a refer to liquid, gas, and air respectively, and where the subscript 2, referring to Zone 2, is omitted for convenience. The terms on the left side are known, except for $\dot{m}_{a\infty}$. Since the chemical mass is conserved,

$$\dot{m}_{\ell} + \dot{m}_{g} = \dot{m}_{\ell o} \qquad (6a)$$

or, defining fractional mass flows $f_{\ell} = \dot{m}_{\ell}/\dot{m}_{\ell o}$, and $f_{g} = \dot{m}_{g}/\dot{m}_{\ell o}$,

$$f_{\ell} + f_{g} = 1 \qquad (6b)$$

The specific enthalpies can be expressed as

$$\begin{aligned} h_{\ell} &= c_{\ell} T \\ h_{g} &= c_{pg}(T-T_{b}) + c_{\ell} T_{b} + h_{\ell g} \\ h_{a} &= c_{pa} T \\ h_{\ell 1} &= c_{\ell} T_{b} \\ h_{g1} &= c_{\ell} T_{b} + h_{\ell g} \\ h_{a\infty} &= c_{pa} T_{\infty} \end{aligned} \qquad (7)$$

where c_{pg} and c_{pa} are constant pressure specific heats of gas and air respectively. T_{∞} is the ambient air temperature and $\dot{m}_{a\infty}$ is the mass flow of ambient air which enters the plume at the beginning of Zone 2. Since the air does not undergo any phase change or chemical reaction, $\dot{m}_{a\infty} = \dot{m}_{a}$, the air mass flow within the plume in Zone 2. Using Eqns. (5) - (7), the energy equation can be rewritten to become

$$\begin{aligned} (T-T_{b})(\dot{m}_{a}c_{pa} + \dot{m}_{g}c_{pg} + \dot{m}_{\ell}c_{\ell}) &= \dot{m}_{a}c_{pa}(T_{\infty}-T_{b}) \;+\; h_{\ell g}(\dot{m}_{\ell} - \dot{m}_{\ell 1}) \qquad (8) \\ \text{depression below } T_{b} &= \text{cooling by air} \;+\; \text{evaporation} \end{aligned}$$

The first term on the right hand side cools the plume if $T_{\infty} < T_{b}$ or warms it if the temperatures are reversed. In either case, it has a minor effect compared to the evaporation term which always cools. So far, we are assuming that only a moderate amount of air is entrained such that only part of the liquid from Zone 1 is evaporated, i.e., from $\dot{m}_{\ell 1}$ to $\dot{m}_{\ell}$. A new equilibrium is established in which the saturation vapour pressure, given by the Clausius-Clapeyron equation, is

$$P_{gs} = \frac{\dot{m}_{g} R_{g} T}{\dot{V}} = P_{\infty} \exp\left(\frac{h_{\ell g}}{R_{g}} \left(\frac{1}{T_{b}} - \frac{1}{T}\right)\right) \qquad (9)$$

where the chemical gas constant $R_{g} = R/M_{g}$. R is the universal gas constant, M_{g} is the chemical molecular weight, and $\dot{V}$ is the total gas volume flow rate in Zone 2. If we use Eqn. (8) to solve for T, and Eqn. (9) to solve for $\dot{m}_{g}$, then the equation of state for the gas mixture can be used to solve for $\dot{V}$, i.e.,

$$\dot{V} = (\dot{m}_{a} R_{a} T + \dot{m}_{g} R_{g} T)/P_{\infty} \qquad (10)$$

The remaining unknown is $\dot{m}_a$. We would like to parameterize it in terms of a small number of principal input conditions. Input conditions are tank temperature and pressure, and orifice diameter. Outputs are liquid fallout rate $\dot{m}_c$ to the surface, and the temperature T_c of the collected liquid. An examination of the data tables of Johnson and Deiner [5] shows that if the liquid release rate $\dot{m}_{\ell 0}$ increases by a factor of 4 or 16 (by doubling or quadrupling the orifice diameter), the fractional liquid capture f_c $(\dot{m}_c/\dot{m}_{\ell 0})$ is practically unaffected. This implies that the air entrainment rate must increase in proportion to $\dot{m}_{\ell 0}$ in order to evaporate the increased liquid flow. Attempts to link entrainment to jet velocity (and hence distance travelled) or to a Weber number were not fruitful. Solving the above equations with $\dot{m}_a \propto \dot{m}_{\ell 0}$, the equilibrium liquid content f_ℓ of Zone 2 plotted against either superheat $(T_0\text{-}T_b)$ or flash fraction f_{g1} was found to be stratified by molecular weight M_g.

A comparison of model and measurements suggests two competing mechanisms for air entrainment. For negligible or low superheat, the emerging liquid begins to evaporate immediately, in proportion to the mass flow. The vapour then acts as a piston which drags in ambient air of density ρ_∞ such that

$$\dot{m}_a \propto \rho_\infty \dot{V}_g \propto \dot{m}_{\ell 0}(M_a T_b)/(M_g T_\infty)$$

For larger superheats, a portion of the emerging liquid boils, increasing the size of the initial vapour cloud in proportion to $f_{g1}\dot{m}_{\ell 0}$. The empirical relations which were both simple and satisfactory for air entrainment were

$$\dot{m}_a = \mathrm{MAX}(\dot{m}_{ae}, \dot{m}_{ab}) \tag{11}$$

where

$$\dot{m}_{ae} = a_1 \dot{m}_{\ell 0} M_a/M_g \tag{12}$$

$$\dot{m}_{ab} = a_2 \dot{m}_{\ell 0} f_{g1}(M_a T_b)/(M_g T_\infty) \tag{13}$$

Equation (12) for $\dot{m}_{ae}$ describes the minimum air flow entrainment caused by evaporation from the non-boiling jet. $\dot{m}_{ab}$ is the more intense air flow entrainment caused by increased evaporation from the boiling jet. Suitable values for the constants a_1 and a_2 were found to be 4 and 40 respectively. The above equations now constitute a complete set. The primary equations (8,9,10,11) describe equilibrium conditions in Zone 2 for T, $\dot{m}_g$, $\dot{V}$, and $\dot{m}_a$.

Up to this point, we have assumed that evaporation in Zone 2 has not completely eliminated the liquid phase. Of course, if enough air is entrained, the liquid phase will disappear. This simplifies the equation set since $\dot{m}_\ell = 0$ and $\dot{m}_g = \dot{m}_{\ell 0}$, eliminating the use of the Clausius-Clapeyron Eqn.(9).

It is worth noting that Eqns. (8) - (10) for an open system of constant mass flow are equally applicable for a closed system of constant mass. The mass flow $\dot{m}$ can be replaced by a mass m, and the volume flow $\dot{V}$ by a volume V.

At this point, it is interesting to examine the effect of the various assumptions in the air entrainment model. From the above equations, we can calculate the fractional liquid mass flow f_ℓ in Zone 2. For the moment, we will assume that the liquid is contiguous or in large droplets and that it all precipitates. This allows us to compare f_ℓ to the measured fractional precipitate f_c in Figures 4. (The solid line contains a droplet model and will be discussed later.) The three dashed lines result from three different air entrainment models. The smallest dashes result from the most basic assumption of gradient-driven evaporation entrapping an air flow in proportion to $\dot{m}_{\ell 0}$. This model shows some skill in predicting f_c at low superheat but contains no information on the steeper portion of the experimental data. The line of larger dashes shows that a significant improvement results from the inclusion of the gas molecular weight as in Eqn. (12). The line of largest dashes comes closer to modelling the data and uses Eqn. (11) which includes increased initial vapour production due to boiling. It is important to realize that the initial vapour-air mixture is not in equilibrium; the air entrainment formulae only serve to establish an initial air mass with which the jet can seek an equilibrium.

The modelling exercise might have terminated here, were it not for a significant disagreement with one of the five chemicals: water (Fig. 4a). The moderate agreement between model and data in Figs. 4b-4e suggests that the equations for Zone 2 are reasonable, that a near-equilibrium state exists, and that the total liquid content is precipitable. Since droplet formation is inevitable, the droplet spectrum must favour large diameters. However, Fig. 4a shows that the Zone 2 water content f_ℓ is much larger than the observed precipitable component f_c. This in turn suggests that the difference $f_\ell - f_c$ is a measure of the fraction of liquid in suspended small droplets. In order to improve the model-data comparison, a droplet model is required.

Droplet model

In general, a liquid jet emerging from a pressurized tank partially breaks into droplets because of mechanical shear and, if superheated, because of the explosive nature of the boiling. The heavier droplets fall out near the source; the lighter ones are carried downstream. Rather than defining a continuous spectrum of droplets, it would be adequate to know the populations of two classes: precipitable and nonprecipitable. Our goal is only to estimate the amount of liquid that collects on the ground, and, by inference, the amount that remains suspended in small droplets.

Let us define f_{d1} and f_{c1} as the fractions of suspended droplets and collectable liquid respectively, formed in Zone 1. Collectable liquid consists of large droplets and contiguous liquid. The fractions are defined as $f_{d1} = \dot{m}_{d1}/\dot{m}_{\ell 0}$ and $f_{c1} = \dot{m}_{c1}/\dot{m}_{\ell 0}$ where $\dot{m}_{d1}$ and $\dot{m}_{c1}$ are the mass flows of fine and heavy droplets respectively. We assume that they are modified in Zone 2 only by evaporation to form analogous mass flows and fractions $f_d = \dot{m}_d/\dot{m}_{\ell 0}$ and $f_c = \dot{m}_c/\dot{m}_{\ell 0}$. They are related to the total liquid content by

$$f_{d1} + f_{c1} = f_{\ell 1} \qquad (14a)$$

$$f_d + f_c = f_\ell \qquad (14b)$$

Experiments show that fine droplet formation is associated with the vigorous boiling of the superheated liquid [4]. At low superheats, the droplets are larger and are created by both hydraulic and flash processes. It is convenient to define a threshold superheat or flash fraction at which small droplet formation begins in Zone 1, i.e.,

$$f_{d1} = a_3(f_{g1} - f_{g1}'),\ f_{g1} > f_{g1}' \qquad (15)$$

where f_{g1}' is the threshold flash fraction. Since the fine droplet mass may not exceed the available liquid mass, a necessary constraint on Eqn. (15) is

$$f_{d1} \leq f_{\ell 1} \qquad (16)$$

Knowing f_{d1}, f_{c1} is given by Eqn. (14a). During evaporation in Zone 2, we assume that all droplets, regardless of size, lose the same fraction of their original mass. The final mass fractions can be written as

$$f_d/f_{d1} = f_c/f_{c1} = f_\ell/f_{\ell 1} \qquad (17)$$

Equation (17) for f_c describes the fraction of liquid that falls out of the jet and which can be collected. This can be compared with the measured data, allowing us to calibrate Eqn. (15) to get $a_3=1.5$ and $f_{g1}'=0.04$. The model results are plotted as solid lines in Figs. 4a - 4e. f_c is similar to f_ℓ (large dash) for four of the chemicals, implying that most of the liquid phase is precipitable. However, f_c is much less than f_ℓ for water. From Fig. 4a, for a flash fraction of 0.17, f_c is seen to be about 0.6, and f_ℓ about 0.8. This implies that the fine droplet fraction is 0.2 and that the vapour fraction is also 0.2. This simple droplet model hinges very strongly upon the water data alone and so must be considered as tentative until more corroborative data are available.

Model results and data for all five chemicals are plotted together in Fig. 1. As a general observation, f_c falls as the chemical boiling point temperature T_b falls, for a given f_{g1}.

Exploring the model further, the fine droplet fraction in Zone 2 is calculated over a wide range of flash fractions and is plotted in Fig. 5. f_d increases initially with f_{g1}, since droplet production increases with boiling. f_d reaches a peak and then decreases since air entrainment, and evaporation, also increase with f_{g1}. The cyclohexane curves of Figs. 4b and 5 show that for f_{g1} = 0.2, f_d peaks at 10% and f_c (model) is at 20%. For f_{g1} = 0.34, all the liquid has evaporated. Three other chemicals behave in a similar way. The plot of f_d for water, on the other hand, shows that something terminates the growth of f_d before it reaches a smooth maximum. This happens at f_{g1} =0.42, at which point the collectable water (large drops) vanishes (Fig. 4a). At this superheat, the flash process converts all the liquid into vapour and fine droplets. For larger superheats, less liquid is available after flashing and so fewer fine droplets are produced. With increasing evaporation, f_d can only decrease.

Effect of relative humidity on evaporation of water

The results for water differ significantly from those of the other chemicals. It is important to establish whether this is due to its physical properties or whether it is due to a model deficiency. One deficiency which seems likely to be important for water but not for the other chemicals is the lack of consideration of ambient relative humidity (RH). The above enthalpy equations have assumed that the ambient flow did not contain any of the chemical being studied. Since evaporation is dominant in the energy balance and since water evaporation will be affected by the ambient RH, its effect should be calculated.

The saturation water vapour pressure in the atmosphere is given by

$$P_{gs}(T_\infty) = P_\infty \exp\left(\frac{h_{\ell g}}{R_g}\left(\frac{1}{T_b}-\frac{1}{T_\infty}\right)\right) \tag{18}$$

where the subscripts g and ℓ in this section will refer only to the phases of water. Defining RH = $P_{g\infty}(T_\infty)/P_{gs}(T_\infty)$, and using the perfect gas law, the mixing ratio $X(T_\infty)$ is found to be

$$X(T_\infty) = \frac{\dot{m}_{g\infty}}{\dot{m}_a} = RH\,\frac{M_g}{M_a}\,\frac{P_{gs}(T_\infty)}{P_\infty} \tag{19}$$

where $\dot{m}_{g\infty}$ is the mass flow of water vapour associated with an ambient mass flow $\dot{m}_a$ of air. Now when $\dot{m}_a$ g s^{-1} of air are entrained (Eqn. 11), a proportional mass flow of water vapour is entrained (Eqn. 19). The enthalpy balance between Zones 1 and 2 is rewritten as

$$\underbrace{\dot{m}_{\ell 1}h_{\ell 1} + \dot{m}_{g1}h_{g1}}_{\text{(pure jet at } T_b)} + \underbrace{\dot{m}_{a\infty}h_{a\infty} + \dot{m}_{g\infty}h_{g\infty}}_{\text{(ambient air at } T_\infty)} = \underbrace{\dot{m}_\ell h_\ell + \dot{m}_g h_g + \dot{m}_a h_a}_{\text{(mixture at } T)} \tag{20}$$

As before, $\dot{m}_{a\infty} = \dot{m}_a$, given by Eqn. (11). The specific enthalpy of the ambient water vapour can be written as

$$h_{g\infty} = c_{pg}(T_\infty - T_b) + c_\ell T_b + h_{\ell g} \tag{21}$$

The total mass flow rate for water in Zone 2 is altered by the entrainment of ambient vapour and is given by

$$\dot{m}_\ell + \dot{m}_g = \dot{m}_{\ell 0} + \dot{m}_{g\infty} \tag{22a}$$

or, in fractional form

$$f_\ell + f_g = 1 + f_{g\infty} \tag{22b}$$

where $f_{g\infty} = \dot{m}_{g\infty}/\dot{m}_{\ell 0}$. Equations (7), (21), and (22a) can be used to rewrite Eqn. (20) as

$$(T-T_b)(\dot{m}_a c_{pa} + \dot{m}_g c_{pg} + \dot{m}_\ell c_\ell) = (\dot{m}_a c_{pa} + \dot{m}_{g\infty} c_{pg})(T_\infty - T_b) + h_{\ell g}(\dot{m}_\ell - \dot{m}_{\ell 1}) \tag{23}$$

These equations, in conjunction with Eqns. (9) and (10) developed earlier, are used to solve for equilibrium mass flows of water (liquid and vapour), some of which comes from humid ambient air. As mentioned earlier, if sufficient air is entrained to evaporate all the water, the equation set is simplified by dropping the Clausius-Clapeyron equation, setting $\dot{m}_\ell = 0$, and determining $\dot{m}_g$ from Eqn.(22a).

As RH increases, a smaller fraction of water from the jet will be able to evaporate. The effect of ambient humidity on collectable water fraction and fine droplet fraction is shown in Fig. 6. The collectable water is not strongly affected by RH. On the other hand, the model shows the suspended droplet fraction to be quite sensitive to RH, especially as f_c becomes small. For RH=0, all liquid phase disappears beyond f_{g1} = 0.72. For RH=1, the added humidity from the atmosphere prevents complete evaporation until well beyond f_{g1} = 1. At first thought, one might think that a water jet entering a saturated atmosphere could not undergo any evaporation. However, the saturated water vapour content of the final mixture is very sensitive to its temperature T. If T exceeds T_∞, some evaporation is possible.

Some computed results for several variables help to complete the picture (Table 1). For T_0 = 474K, and RH = 0, the equilibrium temperature of the saturated mixture is 295K, slightly less than ambient. The mass of air entrained ($f_a = \dot{m}_a/\dot{m}_{\ell 0}$) is 15 times that of the original water jet and causes enormous evaporative cooling from the boiling point (372K after flashing). The increase in vapour fraction in Zone 2 relative to Zone 1 is balanced by the loss in liquid fraction.

For saturated ambient air (RH=1), and T_0 = 474K, the equilibrium temperature is 307K, slightly greater than ambient. Because $T > T_\infty$, the entrained air at temperature T must evaporate some of the liquid from the jet in order to become saturated at the higher temperature. The vapour input $f_{g\infty}$ from the air is significant, i.e., 40% of the original jet. Σ is the sum of all the vapour and liquid fractions in Zone 2. The stagnation vapour pressure P_0 increases rapidly with temperature T_0. At 474K, it is 17.5 atmospheres, near the upper limit of the experiments. For T_0 beyond 570K, the stagnation pressure exceeds 100 atmospheres and so the conditions of large f_{g1} in Fig. 6 are unlikely to be encountered in practice.

Minimum temperature

As air is entrained into a two-phase jet, causing evaporation of the liquid, the temperature will fall until all the liquid is gone. We solve Eqns. (8,9,10,11) for unknowns T, $\dot{m}_g$, $\dot{V}$, and $\dot{m}_a$. Further entrainment will increase the mixture temperature, providing $T_\infty > T$. During this time, we solve Eqns. (8,10,11) for T, $\dot{V}$, and $\dot{m}_a$. The gas flow is fixed at $\dot{m}_g = \dot{m}_{\ell 0}$ (or $\dot{m}_{\ell 0} + \dot{m}_{g\infty}$ for water vapour). Eqn. (9) is not used since the vapour is not saturated.

However, as the last drop of liquid evaporates, the mixture is saturated and T achieves a minimum value T_{min}. The associated variables $\dot{V}$ and $\dot{m}_a$, required to achieve T_{min}, are found by solving Eqns. (8,9,10) in which $\dot{m}_\ell = 0$ and $\dot{m}_g = \dot{m}_{\ell 0}$ (or $\dot{m}_{\ell 0} + \dot{m}_{g\infty}$ for water vapour). By eliminating $\dot{V}$ and $\dot{m}_a$, the temperature T_{min} is expressed implicitly in the relation

$$\frac{P_\infty - P_{gs}(T_{min})}{P_{gs}(T_{min})} = \frac{M_g}{M_a} \frac{(1-f_{g1})h_{fg} - c_{pg}(T_b - T_{min})}{c_{pa}(T_\infty - T_{min})} \qquad (24)$$

For practical applications, relatively small terms can be ignored to give

$$\frac{P_\infty - P_{gs}(T_{min})}{P_{gs}(T_{min})} = \frac{M_g}{M_a} \frac{h_{fg}}{c_{pa}(T_\infty - T_{min})} \qquad (25)$$

This equation differs from that of Fauske and Epstein [6] by the inclusion of the ratio M_g/M_a. After solving iteratively for T_{min}, the associated values of $\dot{V}$ and $\dot{m}_a$ can be readily found.

A summary of all the measured and calculated temperature results is plotted in Fig. 7. The abscissa organizes the experiments by chemical, and by source temperature for each chemical. The chemical with the highest boiling point is on the left (water), descending to chlorine on the right. The model predicts an equilibrium temperature T which can be compared with the temperature T_c of the liquid fallout collected in the pans. The comparison is very good, especially considering that the initial temperature T_0 is anywhere from 50 to 200 degrees higher than the final temperature. T is within a few degrees of T_c in all cases, except for freon where T is 10-15 degrees low. This could be due to heat transfer into the liquid after collection. T (and T_c) is also very close to T_{min} in all experiments.

Plume warming

The measured data which serve as a check against the above theory are the collected mass fallout $\dot{m}_c$ and its temperature T_c. Some of the experiments were done at sufficiently high superheats that $\dot{m}_c$ vanished or almost vanished. Higher superheats should lead to evaporation of suspended droplets and warming of the plume. Alternatively, the process of continued air entrainment as the plume moves downstream will also cause complete evaporation and warming. This is depicted in Fig. 8 for the two chemicals having the greatest separation of their boiling points. Eqns. (8,9,10) were solved for T (and Eqns. (8,10) when $T > T_{min}$) simply by increasing $\dot{m}_a$ without specifying the entrainment mechanism. The chlorine temperature is seen to fall until evaporation is complete at $f_a = 2$. The mixture then warms rapidly towards T_∞. Water shows a similar pattern, except that much more air ($f_a = 100$) is required to evaporate the same mass of water because its heat of vaporization is much larger.

Discussion

Of further interest are Eqns. (12) and (13) for air entrainment. They can be used to show that the ratio of air entrained to the initial amount of gas created by flashing is

$$\dot{m}_a/\dot{m}_{g1} \approx 4M_a/(f_{g1}M_g) \qquad f_{g1} < 0.1 \qquad (26)$$

$$\approx 40M_a/M_g \qquad f_{g1} > 0.1 \qquad (27)$$

Suppose we have a situation in which the top of a storage tank is severely ruptured, exposing the contents to the atmosphere. The equations of this paper can be applied to the stationary mass as explained earlier. Equation (12) is not applicable since it requires a flow to generate the interaction. However, Eqn. (13) is applicable in determining how much air is entrained due to the initial flash. As shown above, $m_a/m_{g1} \approx 40M_a/M_g$. It is interesting that the results of a flow experiment have given such useful information for a non-flow problem. For the latter, of course, the full set of equations must be solved to find the equilibrium conditions after entrainment.

Returning to the jet emission, we can estimate the radius R_a of the cylinder of air drawn into the jet flow. Again, using Eqn. (12), and assuming that the entrained air moves at the speed of the liquid jet,

$$R^2_a/R^2_0 \approx 4\rho_\ell M_a/(\rho_\infty M_g) \quad f_{g1} < 0.1 \qquad (28)$$

$$\approx 40 f_{g1}\rho_\ell M_a T_b/(\rho_\infty M_g T_\infty) \quad f_{g1} > 0.1 \qquad (29)$$

Neglecting molecular weights, and assuming that $\rho_\ell/\rho_\infty \approx 1000$, and $f_{g1} \leq 0.1$, then $R_a/R_0 \approx 60$, where R_0 is the radius of the orifice of the liquid jet.

Conclusions

The model for air-fluid interaction near the orifice of a superheated liquid jet assumes a rapid impulsive entrainment of air into the stream, followed by a slightly less rapid adjustment to equilibrium. The air entrainment is assumed to be proportional to the initial liquid mass flow and to the flash fraction. A droplet model was found to be necessary to explain the quantity of liquid fallout for the water experiments. The droplet model consists of two classes of liquid. It specifies a fine drop fraction, small enough to remain suspended. The fine drop fraction is generated by the flashing superheated jet near the orifice. The remaining liquid, by default, consists of larger droplets and the contiguous liquid stream. These fall to the surface. The thermodynamic system is a box model in which energy exchange among all components and phases is efficient and attains equilibrium within a few metres. The measured data and the model results are in sufficient agreement as to lend support to the empirical theory.

The equilibrium equations for Zone 2 apply equally well to a closed system rather than a flowing system, in which the flow quantities $\dot{m}$ and $\dot{V}$ are replaced by mass m and volume V. The catastrophic rupture of a fixed volume tank in which the superheated contents are exposed instantly to the atmosphere should behave analogously to the rapid evaporation and entrainment of the flow process. Hence, the equations should describe the Zone 2 properties of a finite volume gas cloud. Consequently, most of the initial conditions for application to either a continuous or instantaneous dense gas dispersion model have been established.

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Table 1 Model results for a water jet:

RH = 0, 1; T_0 = 372, 474, 571 K

RH	0.	0.	0.	1.	1.	1.
P_0/P_∞	1.0	17.5	102.0	1.0	17.5	102.0
T_0 (K)	372.	474.	571.	372.	474.	571.
T (K)	295.	295.	293.	306.	307.	305.
T_∞ (K)	300.	300.	300.	300.	300.	300.
$X(T_\infty)$	0.00	0.00	0.00	0.026	0.026	0.026
f_a	6.44	15.16	29.53	6.44	15.16	29.53
$f_{g\infty}$	0.00	0.00	0.00	0.17	0.40	0.78
f_{c1}	1.00	0.59	0.14	1.00	0.59	0.14
f_c	0.86	0.48	0.09	0.92	0.56	0.14
f_{d1}	0.00	0.23	0.50	0.00	0.23	0.50
f_d	0.00	0.19	0.35	0.00	0.22	0.52
f_{g1}	0.00	0.19	0.37	0.00	0.19	0.37
f_g	0.14	0.34	0.56	0.25	0.62	1.12
Σ	1.00	1.00	1.00	1.17	1.40	1.78

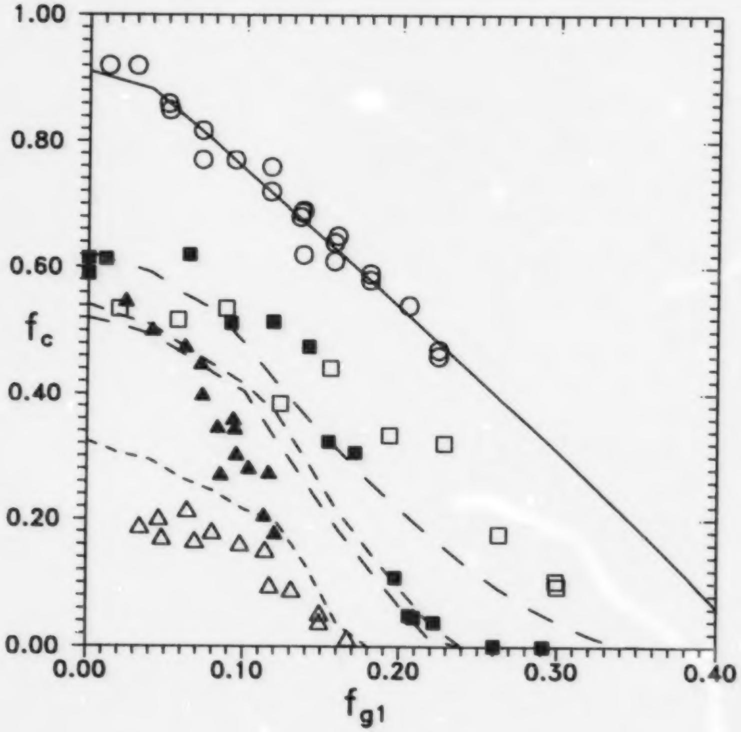

Figure 1 Fraction f_c of initial liquid flow which falls out and is collected in pans. Plotted against flash fraction f_{g1}.

Chemical:	water	cyclohexane	freon	methylamine	chlorine
T_b (K):	371.5	350.2	295.5	264.2	236.4
Data:	○	□	■	▲	△
Model:	———	—— ——	— —	– – – –	------

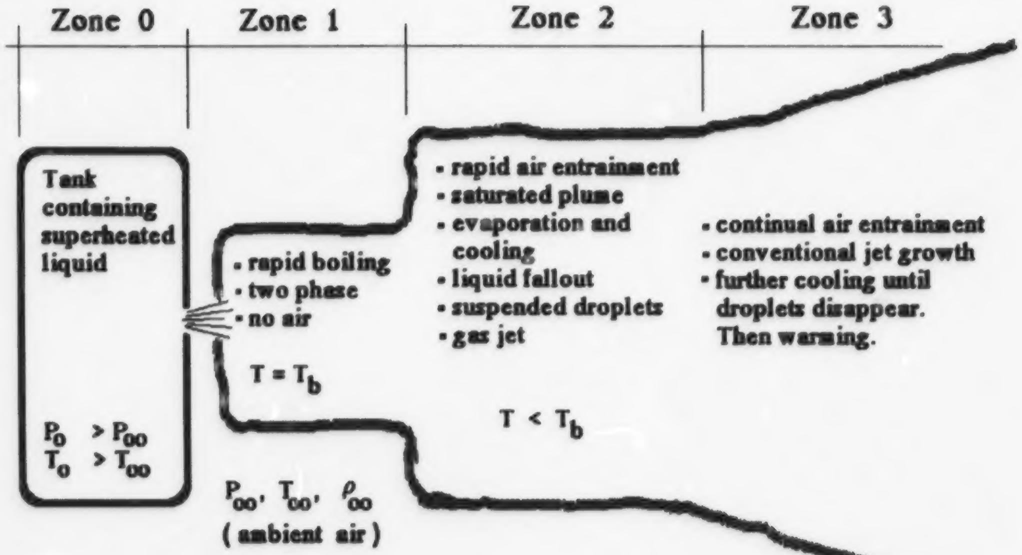
Zone 0
Zone 1
Zone 2
Zone 3
Tank containing superheated liquid
$P_0 > P_{\infty}$
$T_0 > T_{\infty}$
• rapid boiling
• two phase
• no air
$T = T_b$
$P_{\infty}, T_{\infty}, \rho_{\infty}$
(ambient air)
• rapid air entrainment
• saturated plume
• evaporation and cooling
• liquid fallout
• suspended droplets
• gas jet
$T < T_b$
• continual air entrainment
• conventional jet growth
• further cooling until droplets disappear. Then warming.

Figure 2 Stages in the evolution of a superheated liquid jet emerging into the atmosphere.

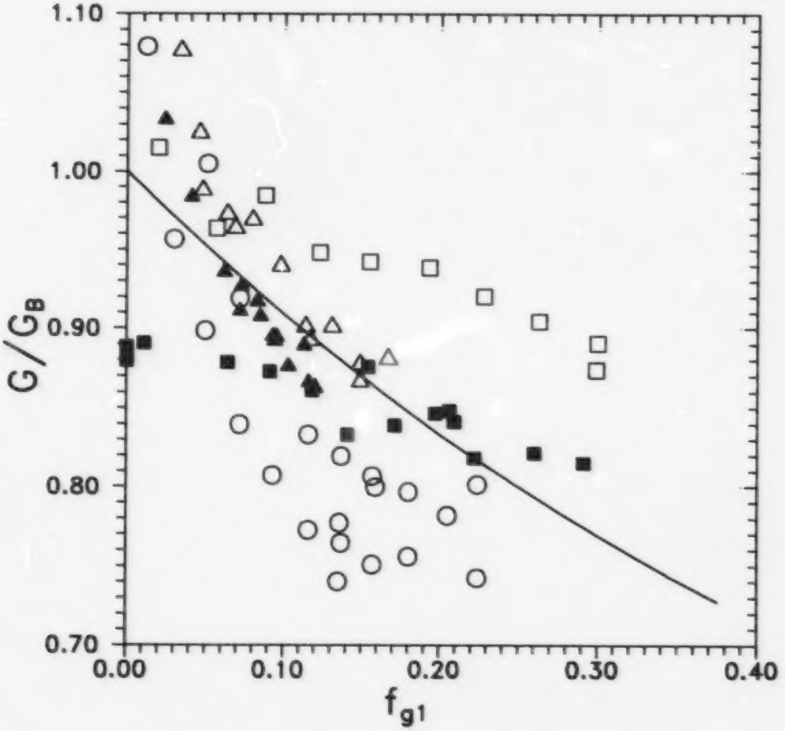

Figure 3 Nondimensional mass flux of liquid from the tank (prior to flashing) vs. flash fraction f_{g1}. Model: (solid line);
Chemical: water cyclohexane freon methylamine chlorine
Data: ○ □ ■ ▲ △

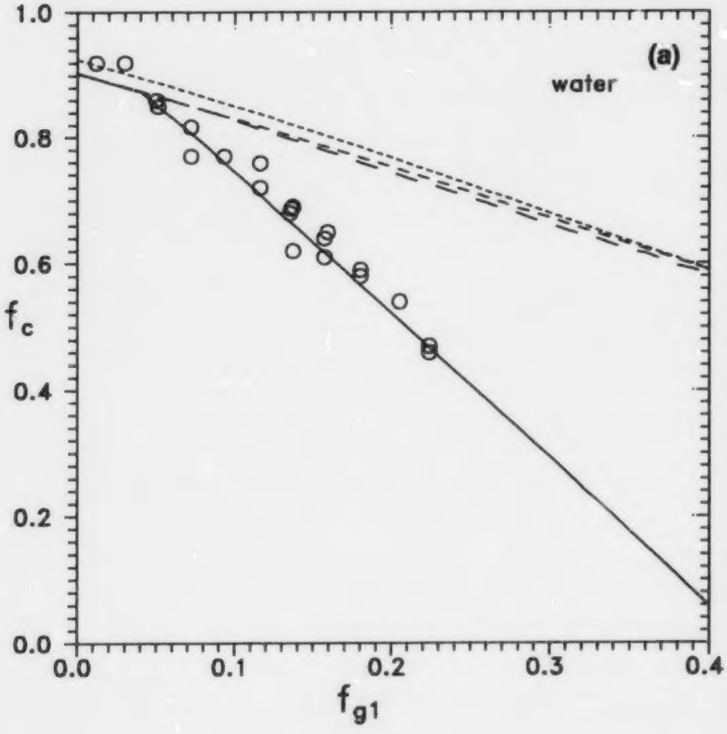

Figure 4a Fractional mass of liquid collected f_c vs. flash fraction. Model: ------- $\dot{m}_a = \dot{m}_{\ell 0}$; — — — — $\dot{m}_a = 4\dot{m}_{\ell 0} M_a/M_g$; — — — Eqn. (11); ——— droplet model; Data: ○.

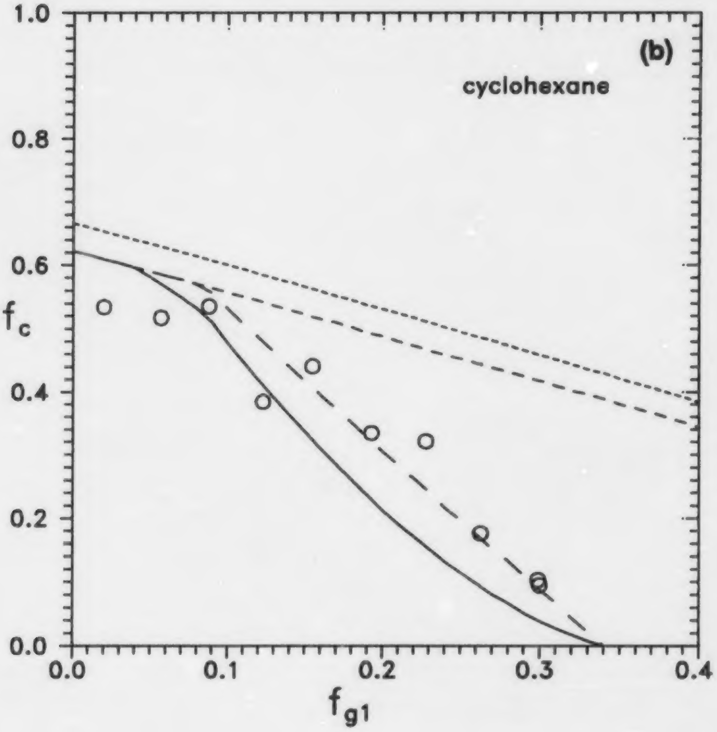

Figure 4b Fractional mass of liquid collected f_c vs. flash fraction. Model: ------- $\dot{m}_a = \dot{m}_{\ell 0}$; – – – – $\dot{m}_a = 4\dot{m}_{\ell 0} M_a/M_g$; — — — Eqn. (11); ——— droplet model; Data: ○.

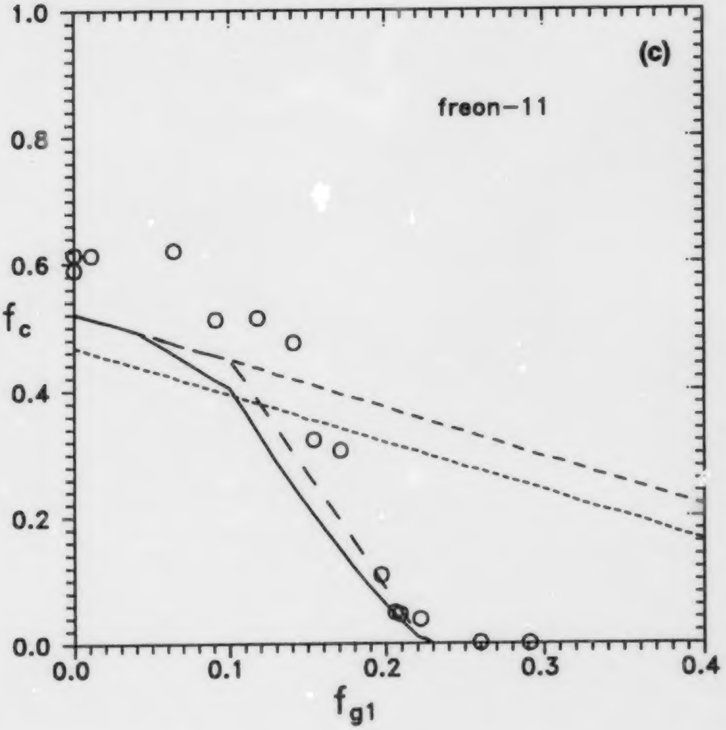

Figure 4c   Fractional mass of liquid collected f_c vs. flash fraction. Model: ------- $\dot{m}_a = \dot{m}_{\ell 0}$; — — — — $\dot{m}_a = 4\dot{m}_{\ell 0}M_a/M_g$; —— —— —— Eqn. (11); ———— droplet model; Data: o.

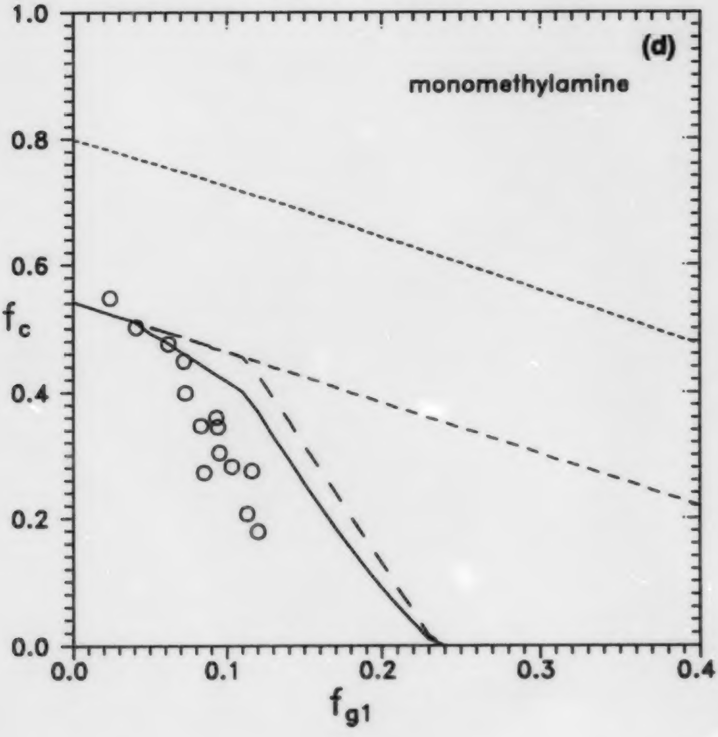

Figure 4d Fractional mass of liquid collected f_c vs. flash fraction. Model: ------- $\dot{m}_a = \dot{m}_{\ell 0}$; — — — — $\dot{m}_a = 4\dot{m}_{\ell 0} M_a/M_g$; — — — Eqn. (11); ——— droplet model; Data: ○.

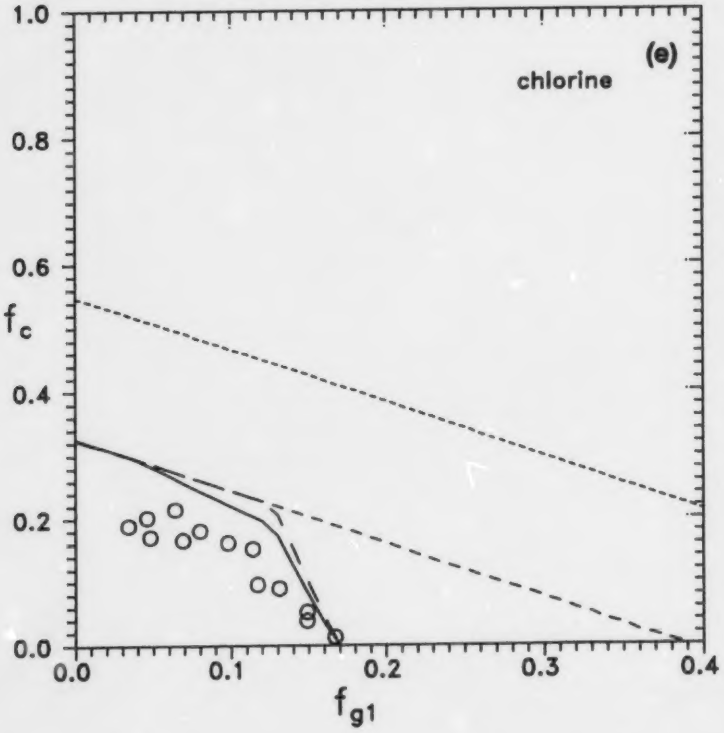

Figure 4e Fractional mass of liquid collected f_c vs. flash fraction.
Model: ------- $\dot{m}_a = \dot{m}_{\ell 0}$; ---- $\dot{m}_a = 4\dot{m}_{\ell 0}M_a/M_g$;
— — — Eqn. (11); ——— droplet model; Data: ○.

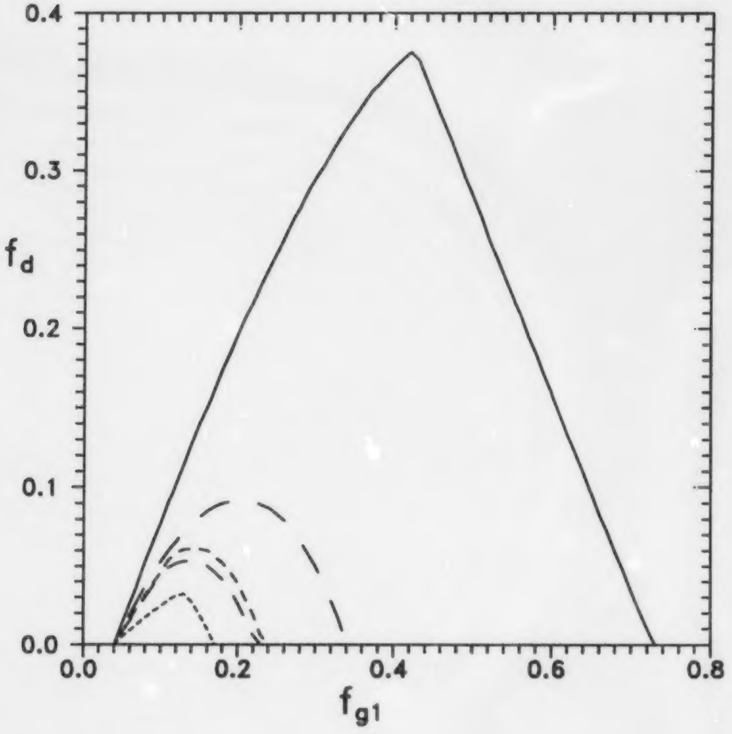

Figure 5 Fine droplet fraction f_d vs. flash fraction f_{g1}.
Chemical: water cyclohexane freon methylamine chlorine
Model: ——— — — — — — — — — ------

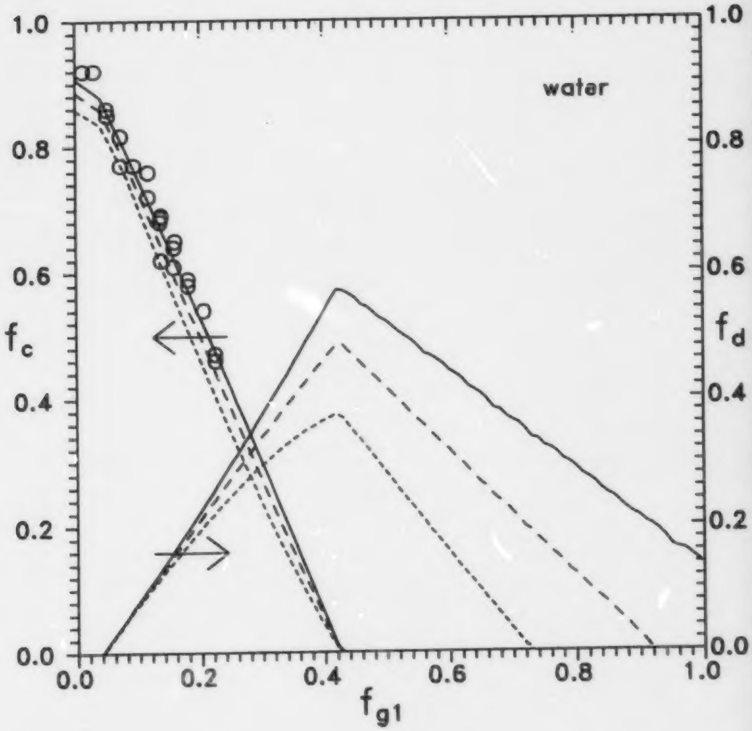

Figure 6 Collectable water fraction f_c and fine droplet fraction f_d vs. flash fraction as a function of relative humidity RH. The data were collected during conditions of $0.85 < RH < 0.95$. ------ (RH=0); — — — (RH=0.5); ——— (RH=1).

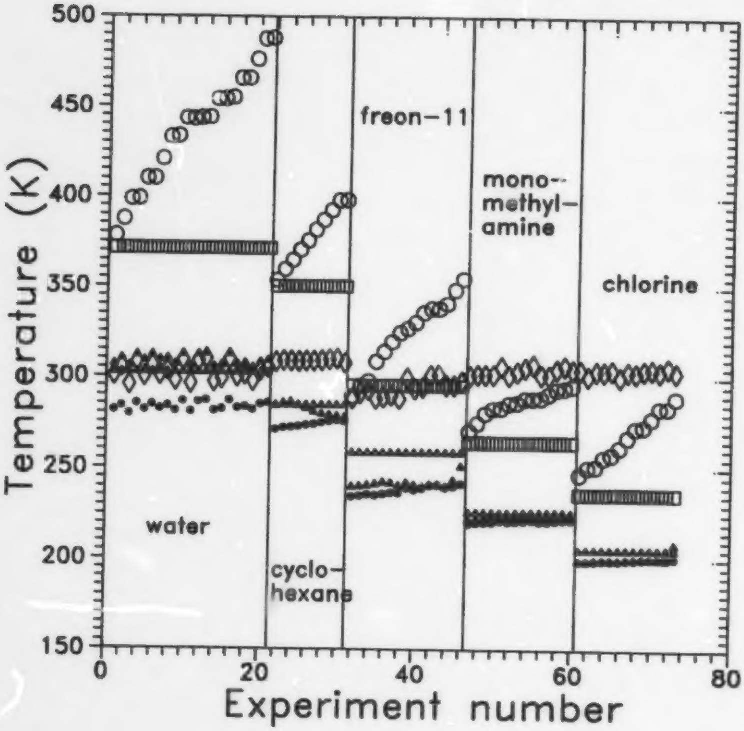

Figure 7 Measured and calculated temperatures relative to the boiling point (□) for 5 chemicals.
Measurements: ○ (T_0); ◊ (T_∞); △ (T_c);
Theory: ▲ (T); ● (T_{min})

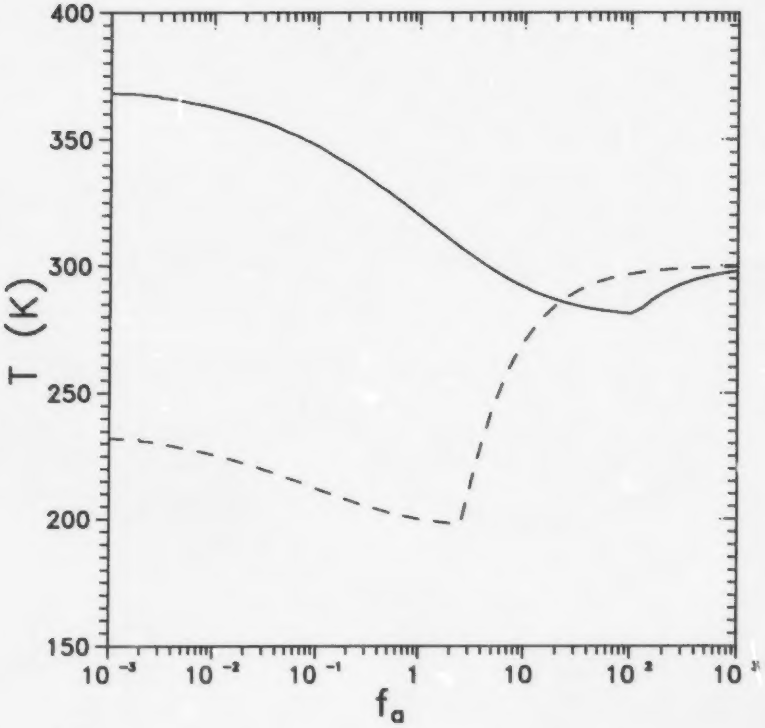

Figure 8 Equilibrium temperature T as a function of air entrained. — — — (chlorine); ——— (water).

THE IMPACT OF CHLORINE ON THE ENVIRONMENT

by

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Abstract

Chlorine belongs to the seventh main group of the periodic table known as the halogens. The chlorine molecule itself is a greenish-yellow gas that is 2.5 times heavier than air. It does not occur naturally. It makes up about 0.0314% of the upper earth's crust where it exists mainly in the form of sodium, potassium and magnesium chlorides. The major proportion is present in the oceans, constituting about 2%.

The most important man-made emissions and releases of chlorine into the environment occur during production, transportation, handling and use. Even though chlorine is used in the manufacture of several chlorinated compounds such as chlorinated aliphatic and aromatic hydrocarbons, organic and inorganic intermediates, plastics, pesticides, the pulp and paper industry is another major consumer of chlorine. The disinfection of drinking and waste water, sewage, biofouling in cooling and power plants represent other important uses of chlorine. The complex chemistry and implications for the environment will also be discussed.

Introduction

It was during the last two decades that the population at large started to realize that uncontrolled widespread use of chemical substances has environmental cost associated with it.

Chemical technology has contributed considerably to the benefit of mankind but at the same time, has resulted in dramatic impact for the environment and human health. Many chemical substances and their derivatives that we now consider indispensable to our standard of living have ultimately found their way into all compartments of the ecosystem, including marine environments, air, soil, as well as sediments, fish, birds, food, human milk, organs and tissues. Chlorine is a case in point.

Chlorine is a greenish-yellow gas, about 2.5 times as heavy as air and belongs to the seventh main group of the periodic table known as the halogens. It therefore behaves in many respects like flourine, bromine and iodine.

Chlorine gas does not occur naturally, but it is found combined with metals in the form of sodium, potassium and magnesium chlorides. Chlorides make up approximately 0.0314% of the upper earth's crust. A substantial portion is found in the oceans which contain about 2% of chloride (1). Some chlorides are also present in the atmosphere in the form of aerosols.

Chlorine gas finds its way into the environment during production and use, as well as accidental releases during transportation and handling. Chemical spills occur very frequently in Canada and in most other countries in the industrialized world. These spills often involve very large volumes of chemicals. Many spills happen while in stationary facilities and only a small proportion occur during tranfers or while in transit. In Canada, between 1974 and 1984, 36 major spills were recorded in the NATES (National Analysis of Trends in Emergencies System) involving 120.97 tons of liquified chlorine (2). According to the DGAIS (Dangerous Goods Analytical Information System) data base (3), there were about 24 major chlorine spills in 1991 (Table 1).

Table 1. Chlorine Spills and Accidents in Canada.

Year	Number of Spills	Quantity (tonnes)
1985	9	2,146.220
1986	18	414,014.370
1987	19	49,802.183
1988	4	9.157
1989	5	0.029
1990	8	11.057
1991	24	-

The eventual fate of chlorine depends on the environmental conditions that prevailed during spill.

Industrially, chlorine is manufactured by the electrolysis of chloride salts(4). Currently, there are three basic types of processes for the production of chlorine, each process representing a different method of isolating the chlorine produced at the anode from the caustic soda and hydrogen produced at the cathode (4). Electrolytic processes currently in use are:

1. the diaphragm cell process (Griesheim cell, 1885).
2. the mercury cell process (Castner-Kellner cell, 1892), and
3. the membrance cell process (1970).

Mercury Cell Process

The mercury cell actually consists of two cells. The brine cell or electrolyzer is a long, slightly sloped trough, containing purified brine (4). At the bottom of this trough is a thin sheet of metallic mercury that flows under the brine and constitutes the cathode (Figure 1). Projecting above the cathode is the anode assembly consisting of horizontal blocks of graphite or titanium-based dimensionally-stable anode (DSA).

During electrolysis, the brine is decomposed by the current passing through the electrodes to produce chlorine gas at the anode. The chlorine gas then leaves the anode assembly for purification.

At the cathode however, sodium ions are discharged to form a dilute sodium amalgam. The amalgam then leaves the cells and flows into the decomposer consisting of vertical steel columns packed with graphite, where it reacts with water to form 50% caustic soda, hydrogen (4), and mercury. The sodium-free mercury is recirculated for reuse. These reactions can be illustrated by the following equations.

Decomposer:

$$\text{Na-Hg} + H_2O \rightarrow NaOH + 1/2\, H_2 + Hg \qquad 1$$

Anode and cathode:

$$2NaCl + 2H_2O \rightarrow \underset{\text{Cathode}}{2NaOH_{(aq)}} + \underset{\text{Cathode}}{H_{2(g)}} + \underset{\text{Anode}}{Cl_{2(g)}} \qquad 2$$

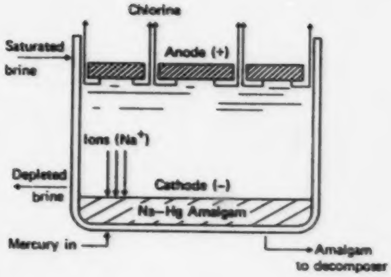
Chlorine
Saturated brine
Anode (+)
Ions (Na+)
Depleted brine
Cathode (–)
Na–Hg Amalgam
Mercury in
Amalgam to decomposer

Figure 1. Mercury Cell

Because of mercury losses, the cathode has to be constantly topped up. The mercury cells pose an environmental hazard because of constant release of mercury into air and also with the effluents into water systems, they are therefore, gradually being phased out. Excessive formation of chloro-organic compounds is also another concern with this process.

Diaphragm Cell Process

In the diaphragm cell process, separation of anolyte from the catholyte is achieved with an asbestos diaphragm. Separation of the chlorine liberated at the anode from the caustic soda with the hydrogen produced at the cathode is maintained with a permeable asbestos-based sheet (4). The diaphragm permits migration of sodium ions to the cathode but restricts back-migration of hydroxyl ions to the anode compartment (Figure 2). One advantage of the diaphragm process is that it allows construction of compact cells with lowered resistance due to closeness of the electrodes.

Purified, saturated brine is fed in at the anode compartment. High voltage and hydrostatic pressure are required on the brine feed to allow a controlled rate of entry into the cathode. As the brine flows through the diaphragm into the cathode assembly, it undergoes electrolysis to produce chlorine, caustic soda and hydrogen according to the following equation:

$$2NaCl + 2H_2O \rightarrow \underset{\text{Anode}}{Cl_2} + \underset{\text{Cathode}}{2NaOH} + \underset{\text{Cathode}}{H_2} \qquad 3$$

A secondary reaction at the anode is the formation of oxygen as a result of decomposition of water and hypochlorous acid. Hence chlorine produced in this process is often contaminated with oxygen. The chlorine is discharged at the dimensionally stable anodes and is collected with some oxygen and small amounts of hydrogen. Sometimes carbon dioxide is also produced as a result of oxidation of the graphite. Sodium ions migrate to the cathode where hydrogen and hydroxide ions are also produced from the electrolysis of water.

The hydrogen is removed from the cell and cooled to remove water. The cell liquor in the cathode contains about 10% caustic soda and 14% sodium chloride. The liquor is then concentrated in multiple effect evaporators to produce a 50% caustic soda, with small amounts of salt.

In the anode compartment, formation of hypochlorous acid is often suppressed by the addition of hydrochloric acid which also neutralizes any hydroxyl ions that have back-migrated. Many chlorinated and unchlorinated pollutants have been identified in the effluents of diaphragm cell plants.

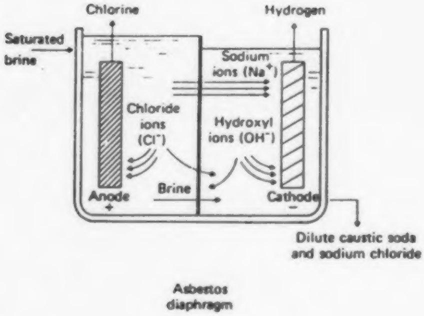
Chlorine
Hydrogen
Saturated brine
Sodium ions (Na⁺)
Chloride ions (Cl⁻)
Hydroxyl ions (OH⁻)
Brine
Anode
+
Cathode
−
Dilute caustic soda and sodium chloride
Asbestos diaphragm

Figure 2. Diaphragm Cell

The Membrane Cell Process

The membrane cell represents a great improvement over the other processes from an environmental point of view (4). Mercury, asbestos, graphite particles, sodium sulphate and sodium chloride often produced in the other processes are all eliminated. Production of chlorinated hydrocarbons is also reduced.

In this process, a cation-exchange membrane such as perfluorocarboxylic acid membrane is used to partition the anode from the cathode assembly. The cation-exchange membrane allows only the hydrated positive ions, the sodium and hydronium ions, into the cathode compartment (Figure 3). The membrane also prevents the hydroxide ions generated in the cathode or chlorine ions in the anode from migrating across.

Saturated brine is fed into the anode compartment but cannot pass through the membrane into the water-filled cathode assembly. Hydrogen is liberated at the cathode from the electrolysis of water. More water is often added to the cathode compartment to maintain a constant concentration. Some of the catholyte stream which constitutes about 21% sodium hydroxide is removed and concentrated. Chlorine gas generated at the anode is collected. In terms of environmental pollution, capital investment and operating costs, the membrane process is preferred.

Uses

The major consumer of chlorine in both Canada and United States is the chemical industry as shown in Table 2 below (5). The largest end use of chlorine is in the production of ethylene dichloride for the manufacture of vinyl chloride monomer, which accounts for about 20% of world chlorine consumption.

Another major use to which chlorine is put, is in the bleaching of wood pulp to produce white paper. Chlorine is also used in the disinfection of drinking and waste water, and control of biofouling in electrical plants. Some of the main end products are as shown in Table 3 below.

The principal reaction for the manufacture of many chlorinated solvents such as chloroform, methylene chloride, and chloromethane is that between chlorine and methane. Chlorination of ethylene produces 1,2-dichloroethane which is a starting material for a variety of products including vinyl chloride, ethylene oxide, ethylene glycol, choral, and tetraethyl lead. Chlorine is also used as a reagent in the synthesis of several organic and inorganic intermediates. For example, the reaction between chlorine and benzene yields chlorobenzenes which are used in the manufacture of pesticides, plastics, aromatic solvents, and in the synthesis of many drugs.

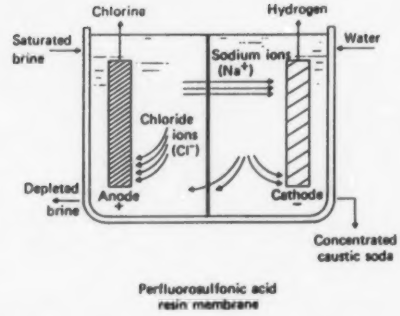
Chlorine
Hydrogen
Saturated brine
Water
Sodium ions (Na+)
Chloride ions (Cl−)
Depleted brine
Anode
+
Cathode
−
Concentrated caustic soda
Perfluorosulfonic acid resin membrane

Figure 3. Membrane Cell

Table 2. CANADIAN DEMAND PATTERN (Kilotonne)

Use	1988	1989	1990
Ethylene dichloride	645.0	670.0	675.0
Pulp and Paper	505.0	450.0	420.0
Mining and Smelting	8.0	7.0	7.0
Water Treatment	19.0	18.0	18.5
Hydrogen Chloride	32.0	29.0	30.0
Aluminum Chloride	12.0	12.0	14.0
Sodium Hypochlorite	13.0	13.0	13.5
Chlorinated Solvents	74.0	72.0	70.0
Propylene Oxide	82.0	83.0	85.0
Miscellaneous	9.7	10.0	9.0
Total Canadian Demand	1,399.7	1,364.0	1,342.0
Export Sales	322.4	322.5	322.5
Total Disappearance	1,763.1	1,686.4	1,644.5

Table 3. Important Reactions of Chlorine and End Uses

Other Reagents	Products	End-Uses
Methane and fluorine	Chlorofluorocarbons	chlorinated solvents, refrigerants, aerosols
Methane and silane	Methylchlorosilane	Silicones, silicone rubber
Ethylene	PVC, dichloroethane	plastics, solvents
Propylene	Propylene oxide	polyethers, varnishes, foams
Butadiene	Chloroprene	Chlorinated rubber
Carbon monoxide	Isocyanate, polycarbonate	polyurethane, plastics
Paraffin and sulphur dioxide	alkylsulphonates	detergents
Benzene	Chlorobenzenes	plastics, dyestuffs, insecticides, pesticides
Sodium hydroxide	Hydrazine, bleaching solutions	Plant protection, disinfectants, bleaches
Phosphorus, sulphur,	Sulphur chlorides Phosphorus chlorides	Plant protection
Titanium oxide (rutile)	pigment	white pigment enamel
Hydrogen	Hydrochloric acid (ultra pure)	Water treatment

Some Chemical Reactions of Chlorine of Environmental Significance

Chlorine is a very reactive element and its chemistry is extremely complex simply because the actual products of chlorination in raw water can never be predicted. The products that are formed, as well as their concentrations, not only depend on the chemical constituents of the water which varies with the origin and time of the year, but also on the amount of chlorine added, temperature, pH, and reaction time. The reactions of dry chlorine are very different from those of wet chlorine. Chlorine can undergo four main types of reactions:

1) Hydrolysis

When chlorine is added to water, it rapidly hydrolyses to produce hypochlorous and hydrochloric acids (6-8). The hypochlorous acid is rather unstable and generally regarded as the major reactive species often assuming the role of an electrophilic reagent which can react with several naturally occuring compounds to form a wide variety of organochlorine compounds. However, addition of chlorine to seawater does not result in the formation of hypochlorous acid but hypobromous acid due to high concentration of bromide ions in seawater (Figure 4). Hypobromous acid is far more reactive than the sister hypochlorous acid. Hypochlorous acid and the hypochlorite anions are often referred to as free residual chlorine and are very toxic. The reactions of chlorine with water, and that of bromide with hypochlorous acid are as illustrated by the following equation:

$$Cl_2 + H_2O \rightarrow HOCl + HCl \qquad 4$$

$$Br^- + HOCl \rightarrow HOBr + Cl^- \quad \text{(seawater)} \qquad 5$$

2) Addition Reactions

Dry chlorine and wet chlorine (hypochlorous acid) will react with organic substances containing double or triple bonds to yield vicinal dichlorides and chlorohydrins respectively (6-10. For example, hypochlorous acid will react with fatty acids in lipids such as oleic acid at pH 2-10, to produce 9-chloro-10-hydroxystearic acid, while dry chlorine will produce a mixture chlorinated products.

Fatty acids

$CH_3(CH_2)_7\ CH{=}CH\ (CH_2)_7\ COOH\ +\ HOCl$ 6

Oleic acid

↓

$CH_3(CH_2)_7\ CHCl\text{-}CHOH\ (CH_2)_7\ COOH$

9-Chloro-10-hydroxystearic acid

$CH_3(CH_2)_7\ CH{=}CH\ (CH_2)_7\ COOH\ +\ Cl_2$ 7

Oleic acid

↓

$CH_3(CH_2)_7\ CHCl\text{-}CHCl\ (CH_2)_7\ COOH$

9,10-dichlorostearic acid

3) Oxidation Reactions

As has been pointed out, chlorine is a strong oxidizing agent. Oxidation is the most predominant type of reaction that occurs between hypochlorous acid and all the natural-occuring, organic constituents of water and wastewater (6-10). The most common example in this group, is the oxidation of alcohols, phenols and aldehydes to their corresponding ketones, aldehydes or acids.

$RCHO + HOCl \rightarrow RCOOH + H^+ + Cl^-$ 8

$RCHOHR^1 + HOCl \rightarrow RCOR^1 + H_2O\ H^+ + Cl^-$ 9

4) Substitution Reactions

Both wet and dry chlorine react with many aromatic, aliphatic and amino

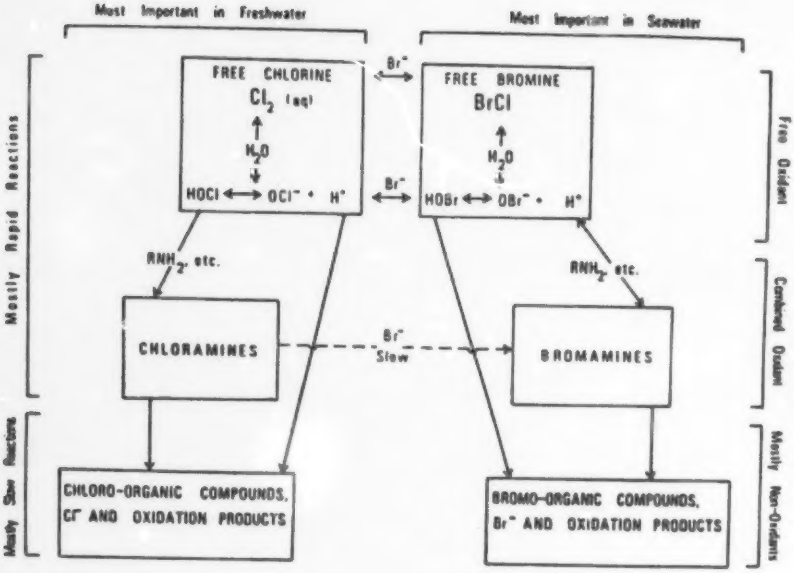
Most Important in Freshwater
Most Important in Seawater
Mostly Rapid Reactions
Mostly Slow Reactions
FREE CHLORINE
Cl2 (aq)
H2O
HOCl ⟷ OCl⁻ + H⁺
Br⁻
FREE BROMINE
BrCl
H2O
HOBr ⟷ OBr⁻ + H⁺
Free Oxidant
RNH2, etc.
RNH2, etc.
Combined Oxidant
CHLORAMINES
Br⁻
Slow
BROMAMINES
CHLORO-ORGANIC COMPOUNDS, Cl⁻ AND OXIDATION PRODUCTS
BROMO-ORGANIC COMPOUNDS, Br⁻ AND OXIDATION PRODUCTS
Mostly Non-Oxidants

Figure 4. **Reactions of Chlorine in Aqueous Solutions**

constituents in water or in air, often replacing the hydrogens (6-10). Formation of chloramines, trihalomethanes, and other chlorinated organic compounds during natural water chlorination and wastewater treatment are the result of substitution reactions as illustrated by the following equations:

$$RNH_2 + HOCl \rightarrow RNHCl + H_2O \qquad 10$$

Further substitution can occur to give the di- and trichloramines.

$$RCOCH_3 + 3HOCl \rightarrow RCOOH + CHCl_3 + 2H_2O \qquad 11$$

Disinfection of Water by Chlorination

Natural water contains a high concentration of organic constituents known as humic substances (8-13). It has been reported that humic substances make up to 60% of total dissolved organic carbon in natural water. Humic substances are stable, non-crystalline, acidic, darkly coloured, mostly aromatic, hydrophilic, biogenic, polyelectrolytic macromolecules with no definite molecular chemical composition . They constitute the bulk of organic matter in most soils. Molecular weights ranging from few hundreds to several millions have been reported. Humic substances contain carbon, hydrogen, nitrogen, sulphur, and oxygen as major elements, with carbon and oxygen being the most predominant. The three main components of humic substances are humic acid, fulvic acid, and humin. All three are very similar to each other but they differ in molecular weight. The synthesis of humus (fulvic acid) is thought to be from plant residues, the most important precursors being proteins, lignin, carbohydrates and some other metabolic products from dead and living microorganisms (Figure 5).

Several structures have been proposed for humic and fulvic acids. Some samples are shown below (Figure 6-13). It has been reported that up to 50% of aliphatic structures in humic acid and fulvic acid consist of n-fatty acids esterified to phenolic hydroxyl groups. According to one current theory (12), humic acid consists of micelles of a polymeric nature, the basic unit being, a di- or trihydroxyphenol bridged by an -O-, $-CH_2-$, -NH-, -N =, -S-, and other groups, and containing both free hydroxyls, and double linkage of quinones.

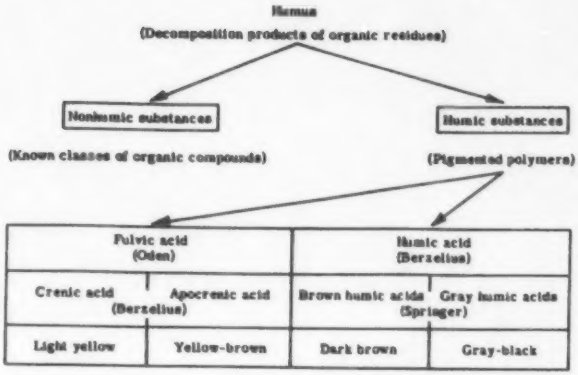
Humus
(Decomposition products of organic residues)
Nonhumic substances
(Known classes of organic compounds)
Humic substances
(Pigmented polymers)
Fulvic acid
(Oden)
Humic acid
(Berzelius)
Crenic acid
Apocrenic acid
(Berzelius)
Brown humic acids
Gray humic acids
(Springer)
Light yellow
Yellow-brown
Dark brown
Gray-black

Figure 5. Different Fractions of Humus

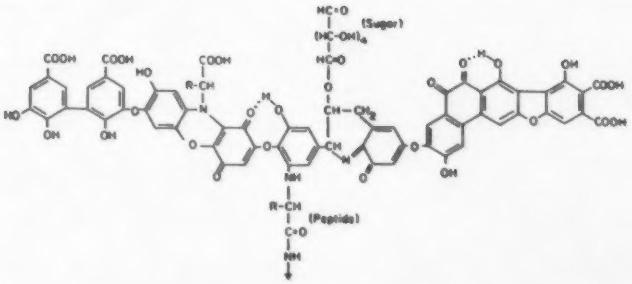
HC=O
(Sugar)
(HC-OH)4
HC=O
COOH
COOH
COOH
HO
R-CH
N
O
H
CH-CH2
CH
N
NH
R-CH
C=O
NH
(Peptide)
HO
OH
OH
OH
COOH
COOH

Figure 6. Humic Acid (Stevenson, 1982)

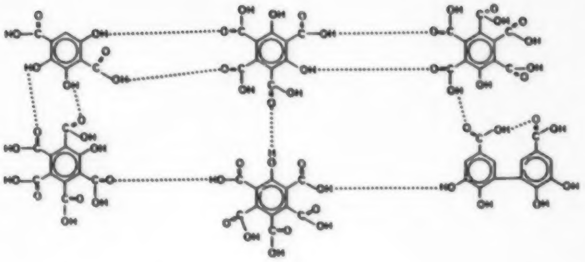

Figure 7. Humic Substances (Gamble and Schnitzer, 1974)

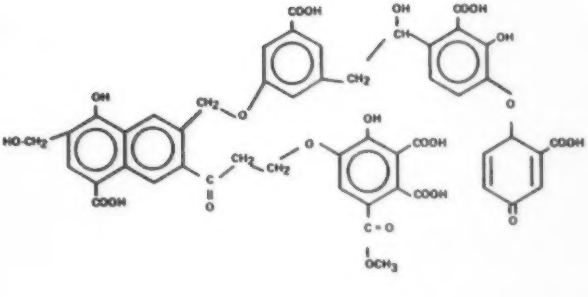

Figure 8. Fulvic Acid Mixture (Gamble and Schnitzer, 1973)

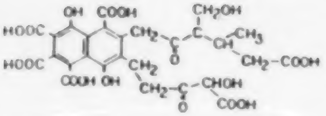
OH COOH
HOOC
HOOC
COOH OH
CH2
CH2
CH2OH
C
CH3
CH
CH2-COOH
CH2-C-CHOH
O
COOH

Figure 9. Fulvic Acid (Buffle, 1977)

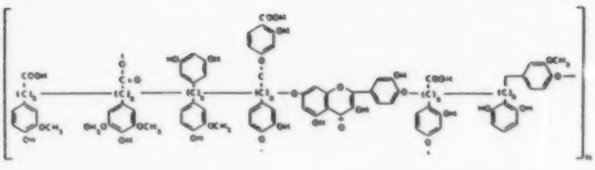

Figure 10. Humus Molecule (Christman and Ghassemi, 1966)

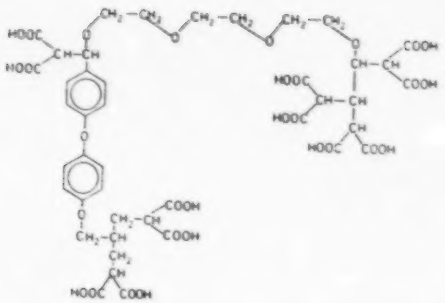

Figure 11. Humic Substances (Bergmann, 1978)

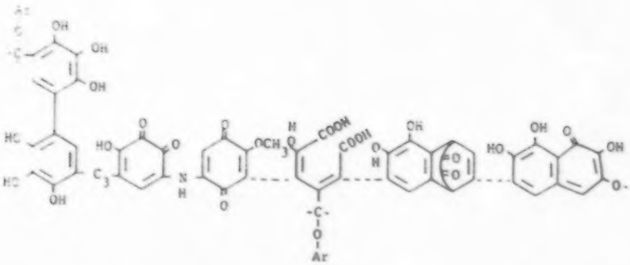

Figure 12. Humic Acid (Flaig, 1960)

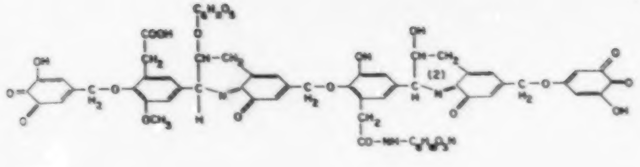
C6H11O5
COOH
OH
CH2
CH-CH2
OCH3
(2)
CO-NH-C

Figure 13. Humic Acid (Dragunov, 1966)

Given the nature of reactivity of chlorine, addition of chlorine to raw water that usually contains humic substances will result in a plethora of products. A number of reactions that can take place between chlorine and humic substances are as shown below (Figure 14). These reactions have been briefly described already.

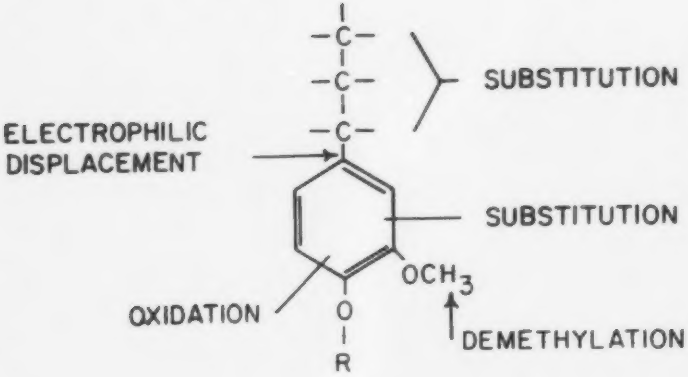
SUBSTITUTION
ELECTROPHILIC DISPLACEMENT
SUBSTITUTION
OCH3
OXIDATION
O
R
DEMETHYLATION

Figure 14. Reactions of Chlorine with Humic Substances

Occurence of trihalomethanes, halogenated and non-halogenated aromatics and phenols, carboxylic acids in chlorinated drinking, waste, and cooling water, sewage, and pulp mill effluents.

Many investigators have shown the occurrence of the trihalomethanes in chlorinated drinking water to arise from the reaction of chlorine with humic substances which are present in varying concentrations in natural waters. Many pathways have been proposed, all embodying two or more distinct stages to arrive at the final products: a) formation of di- or trihalogenated compounds, mostly resorcinol, b) degradation, leading to halogenated C_2 to C_5 compounds.

One postulate proposes the formation of a semiquinoid type monochloro radical ion which on further chlorination, followed by oxidation yields ketone 2 (Figure 15). Hydroxide attack on the carbonyl of ketone 2, followed by ring opening produces compound 4 (8). Compound 4, on treatment with acid, decarboxylates to give 5 which can undergo the haloform reaction to produce chloroform, or undergo bond cleavage as shown to produce methylene chloride, and other not yet identified products. In a similar manner, the formation of other by-products of water chlorination has been explained. However, a large number of the by-products has not been characterized yet. The mechanism is illustrated below (Figure 16):

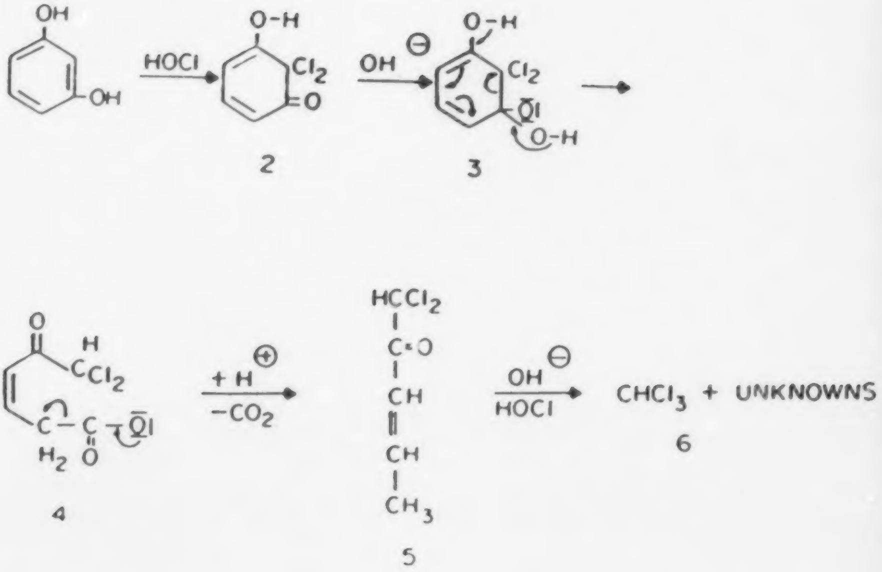
OH
OH
HOCl
O-H
Cl2
O
2
OH
O-H
Cl2
O
O-H
3
O
H
CCl2
C
C
O
H2
O
4
+ H
−CO2
HCCl2
C=O
CH
CH
CH3
5
OH
HOCl
CHCl3 + UNKNOWNS
6

Figure 15. Proposed Reaction Pathway for the Formation of Chloroform from the Chlorination of Resorcinol.

Occurence of trihalomethanes, halogenated and non-halogenated aromatics and phenols, carboxylic acids in chlorinated drinking, waste, and cooling water, sewage, and pulp mill effluents.

Many investigators have shown the occurrence of the trihalomethanes in chlorinated drinking water to arise from the reaction of chlorine with humic substances which are present in varying concentrations in natural waters. Many pathways have been proposed, all embodying two or more distinct stages to arrive at the final products: a) formation of di- or trihalogenated compounds, mostly of resorcinol, b) degradation, leading to halogenated C_2 to C_5 compounds.

One postulate proposes the formation of a semiquinoid type monochloro radical ion which on further chlorination, followed by oxidation yields ketone 2 (Figure 15). Hydroxide attack on the carbonyl of ketone 2, followed by ring opening produces compound 4 (8). Compound 4, on treatment with acid, decarboxylates to give 5 which can undergo the haloform reaction to produce chloroform, or undergo bond cleavage as shown to produce methylene chloride, and other not yet identified products. In a similar manner, the formation of other by-products of water chlorination has been explained. However, a large number of the by-products has not been characterized yet. The mechanism is illustrated below (Figure 16):

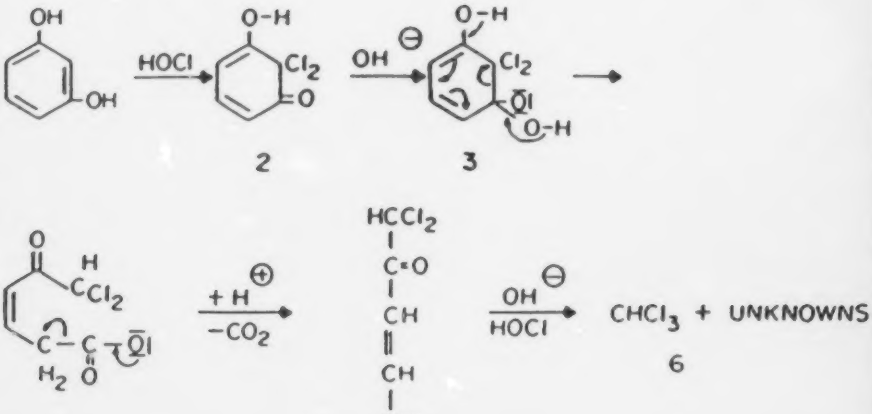

Figure 15. **Proposed Pathway for the Formation of Chloroform from the Chlorination of Resorcinol.**

Another theory postulates the formation of diketo 10, which ring opens on hydroxl attack, and then undergoes bond cleavages to give methylene chloride, dichloroacetic acid, chloroform, or trichloroacetic acid as below (8) (Figure 16).

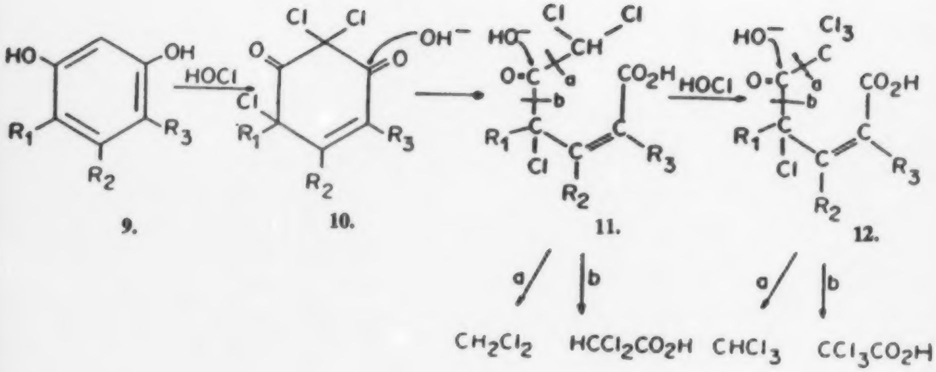
HO
OH
R1
R3
R2
HOCl
9.
Cl Cl
O
O
Cl
R1
R3
R2
10.
OH⁻
HO
Cl
CH
Cl
O=C
a
b
CO2H
R1
C
Cl
C
C
R3
R2
11.
HOCl
HO
Cl3
C
O=C
a
b
CO2H
R1
C
Cl
C
C
R3
R2
12.
a
b
a
b
CH2Cl2
HCCl2CO2H
CHCl3
CCl3CO2H

Figure 16. Chlorination of Resorcinol moiety in Humic Acid

Below is a list of known or suspected carcinogens that have been detected in samples of finished (chlorinated) drinking water (14). Others on the right of table are being investigated. Most of these substances are also found amongst others in chlorinated waste, sewage, cooling water, and of course, in pulp mill effluents.

Table 4. Compounds that occur in Drinking Water as a result of Chlorination

Known or Suspected Carcinogens	Under Investigation
Chloroform	Trichloroacetic acid
Bromodichloromethane	Trichloroacetaldehyde
Chlorodibromomethane	Chlorophenols
Bromoform	Chlorobenzenes
Dichloromethane	α-Chloroketones
Bis(2-chloroethyl) ether	Chlorinated aromatic acids
Trichloroethylene	Chlorinated purines
Tetrachloroethylene	Chlorinated pyrimidines
Chlorophenols	Non-halogenated compounds

The department of National Health and Welfare, Canada, has recommended a maximum acceptable value of 350 μg/l for trihalomethanes in drinking water (15). The U.S. EPA recommendation is 100 μg/l. Risk estmates for exposure to trihalomethanes at this concentration based on two liters of water per day for a 70 kg man is 1 in 2.5 million per year. Chloroform provides the most cancer risk.

Food chlorination is another source by which chlorinated and non-chlorinated organics enter the human body. Chlorine is used to treat cake flour to prevent crumbling on removal from the oven(16). It has been estimated that over 1.5% of the total flour production in the United Kingdom is chlorinated. Trihalomethanes have also been detected in human milk and serum (17). Levels detected are 0.30 ± 0.032 μg/ml for human milk, and 0.88 ± 0.012 μg/ml for the serum, thus showing the extensive burdens of these trihalomethanes in the human body (16).

Table 5. **Trihalomethanes Levels in Canadian Drinking Water Resulting from Chlorine Treatment.**

Contaminant	Concentration Range (mg/l x 10^{3})	Concentration Average (mg/l x 10^{3})
Chloroform	0 - 121 0 - 150 [a]	22.7 30.8 [a]
Bromodichloromethane	0 - 33 0 - 44[a]	2.9 3.1[a]
Chlorodibromomethane	0 - 6.2 0 - 7.0 [a]	0.4 0.4 [a]
Bromoform	0 - 1.0	0.1

a - measurement by direct injection;
others by gas sparge

Effects of Pulp and Paper Mills Bleaching with Chlorine on the Environment

Many studies (18-22) have reported that a large majority of pulp mills using chlorine for bleaching discharge effluents that are acutely lethal to fish especially at point of discharge (23-28). On many occasions, effluents discharged into river do not dilute rapidly enough and kills of aquatic animals have been observed at locations far away from point of discharge. In 1989, Canadian pulp mills using chlorine, bleached 678 tons of pulp per mill a day. An estimation of organic chlorine compounds discharged into the receiving waters was about 86,000 tons. Extremely high levels of dichlorophenols, trichlorophenols, trichloroguaiacol, and tetrachloro guaiacol have been detected in fish in the vicinity of effluent discharges.

Chloroorganic compounds are formed when chlorine used in bleaching the pulp, reacts with components of the wood and humic substances during the pulping step. These pollutants are discharged with the effluents into the aquatic environment. Some of these effluents have been found to be lethal even at concentrations as low as 3.2% of the effluent. Chronic effects including gross deformities, embryo and larval mortalities, behavioural modifications, and reproductive abnormalities have been documented even at very low concentrations of effluent.

Environment Canada estimates that 100 to 150 grams per year of 2,3,7,8-tetrachlorodibenzodioxin and 2000 to 3000 grams per year of 2,3,7,8-tetrachlorodibenzofuran are discharged in bleached pulp mill effluents. It is estimated that only 10-40% of small chlorinated organic compounds in bleached pulp mill effluents have identified. Some of the other substances detected are: chlorinated phenols, chlorinated acids, alcohols, aldehydes, ketones, sugars, aliphatic and aromatic hydrocarbons, trihalomethanes, chlorobenzenes, aromatic thio ethers,. Reader should consult reference (23) for a full listing of compounds found in bleached pulp mill effluents. Concentrations of individual chlorinated compound such as dichlorophenol, trichlorophenol, trichloroguaiacol, and tetrachloroguaiacol have been measured at 23%, 29%, 50%, and 95% of their respective LC_{50}s (Table 6 and Figure 17).

Table 6. Concentration Range and LC_{50}s of Bleached Pulp Mill Compounds found in Biologically-treated Effluents from Kraft Pulp Mills

Compound	96 h LC_{50} (ppb)	Effluent Conc.	Reference
2,4-Dichlorophenol	2800	9-15	23
Dichloroguaiacols	2300	22-100	23, 84
Dichlorocatechol	500-1000	12-90	23, 84
2,4,6-Trichlophenol	450-2600	1-51	23
Trichloroguaiacols	700-1500	10-340	23, 85
Trichlorocatechols	1000-1500	120-270	23, 84
Tetrachlorophenol	500	-	86
Tetrachloroguaiacol	200-1700	10-620	23, 85
Tetrachlorocatechol	400-1500	22-420	23, 86
Pentachlorophenol	200	-	86
Dehydroabietic acid	500-2000	-	87
Chlorodehydroabietic acid	600-900	10-750	23, 87
Dichlorodehydroabietic acid	600-1200	10-420	23, 85

Toxicological effects (29-52) of these effluent chloroorganics on fish and crustaceans include reduced gonad size, disorientation, high level of embryo and skeletal deformities, high parental and larvae mortality, steroid hormone imbalance, many physiological dysfunctions, disruptions in enzyme levels, liver enlargement, and fin and gill erosion.

Chlorine Emission from Smoke Stacks and Accidental Releases

When chlorine is released into the air, it is quickly dispersed and at a faster rate by air motion if a strong wind is blowing. It is always safe to stay upwind and avoid low-lying areas since chlorine is heavier than air. Under wet conditions it is quickly hydrolysed, or in bright sunlight it is photolysed to chlorin radicals (53).

Many studies have shown that chlorine, and many of its derivatives including chlorofluorocarbons can be transformed into a variety of compounds mostly through oxidation, and photolysis by visible solar radiation to produce oxidized species and chlorine radicals respectively (54-61). Chlorine radicals are of great interest because they have been specially implicated in the depletion of the ozone layer as shown with the following equations:

$$RCl + h\nu \rightarrow R. + Cl. \qquad 12$$

$$Cl_2 + h\nu \rightarrow 2Cl. \qquad 13$$

$$HCl + OH. \rightarrow Cl. + H_2O \qquad 14$$

$$1/2Cl_2 + O_2 + M - ClOO + M \qquad 15$$

$$Cl. + O_3 \rightarrow ClO. + O_2 \qquad \text{ozone removal step} \quad 16$$

$$Cl_2F_2C + h\nu \rightarrow Cl. + .ClF_2C \qquad \text{etc.} \quad 17$$

Increased ambient concentrations of organochlorine compounds including chlorofluoromethanes (freons), carbon tetrachloride, and chloroorganic compounds constitute a great hazard to the ozone layer. The chlorofluorocarbons radicals are very stable and can persist for very long time.

Toxicological Effects

Chlorine and hydrogen chloride are extremely irritating to the eyes, skin and mucous membranes. The respiratory tract and the eyes are always the main targets organs because of the strong affinity of these gases for water (69). It has been suggested that chlorine exerts its effects by the formation of hydrogen chloride or by the oxidation of mucous membranes and tissues.

Barrow et al., 1977, have shown chlorine gas to be 33 times more irritating than hydrogen chloride gas (62). These authors have suggested a threshold limit range for human exposure to hydrogen chloride gas as 3-31 ppm. Madile et al., have in addition indicated that the upper limit might be harmful in case of chronic exposures for long periods of time. Several investigators have also reported, when rabbits were exposed to hydrogen chloride, cessation of mucociliary activity, induced local sarcomas, necrosis of tissues at point of contact, respiratory difficulties, eye and nasal irritation, and death in many animals (63-65). On inhalation, death of laboratory animals has often been caused by respiratory injury, such as pulmonary oedema, emphysema and atelectasis.

Symptoms of chlorine poisoning in human on accidental release include burning sensation in the throat, bronchitis, coughing, cyanosis, subnormal temperatures, pneumonia, asthma-pneumonia, dyspnoea, expectoration, physical changes in lungs, pulmonary oedema, palpable and painful liver, difficulty in breathing, multiple pulmonary thrombosis, glomerular capillary thrombosis, and multiple and confluent brain haemorrhages (70,72-75).

Some investigators have reported the prevailence of chronic obstructive pulmonary disease in chlorine gas workers (67,68,71,77-80). They also indicated that the additive effect of smoking and exposure to chlorine is much worse than either agent.

Conclusion

The toxicological effects of chlorine and its derivatives are not only detrimental to the survival of aquatic species, but also threatens the integrity of the ecosystem and ultimately our existence on this planet. However, chlorination will remain a predominant method of disinfecting natural water for drinking, waste water, sewage, and controlling biofouling in power plants. We have to continue to be environmetally protective without disallowing many of the advantages accruing from the use of chlorine.

Several investigators have started to study some of the possible alternatives to chlorine (81-83). Ozone has been considered a good alternative to chlorine and its chemistry has been studied extensively. More research is needed before ozone could be accepted as viable. Products of ozonolysis are mostly oxygenated compounds that are not volatile and very hydrophilic. Very little is known about the toxicity of these highly oxygenated products. Another alternative to chlorine disinfection is irradiation with ultra violet light. Experiments with ultra violet light have shown that this technique is not as effective as chlorine disinfection. Chlorine dioxide has been found to produce less chloroorganics, while the use of peroxides are still being studied. For these alternative methods to be viable, their efficacy and safety must be evaluated and compared with those chlorine.

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A method to evaluate the barrier properties of protective clothing used in environmental clean-ups

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Today it is inevitable for environmental agencies to deal with the chemical emissions and spills as a result of increased industrial activities. In their role of responding to potential or actual hazardous chemical discharges, environmental response personnel and inspectors must have adequate protection equipment and procedures to ensure their safety. The hazards associated with chemicals require a wide range of personnel protection. Extensive testing has shown [Stull, 1987] that a large number of chemicals permeate through most commonly used protective clothing materials by molecular diffusion. Quantitative information about the protection times at different situations is crucial to the use of this protective equipment. Since most protective clothing is made of polymeric material, the evaluation of the permeative properties of different gases and liquids in different polymeric films is of substantial importance to obtain such information. On the other hand, the experimental determination of diffusion properties for a solvent-polymer system is usually a time consuming and expensive task, as a result of the slow diffusion rate in such systems. It is therefore of great importance to develop a method to evaluate reliably the permeative properties of a solvent-polymer system with minimum experimental effort.

An important feature of molecular diffusion of gases and liquids in rubbery polymers is that the rate of diffusion depends closely on the size and shape of the diffusant. It is therefore possible to predict the permeation rate of a solvent-polymer system based on the geometrical properties of the solvent and on the physical properties of the polymer. The key to such predictions is the availability of a parameter which characterizes the effect of structural properties of the solvent on diffusion for solvents with a variety of sizes and shapes.

A convenient and successful approach is the application of the free volume concept to the description of diffusion phenomena of solvents in polymers. In the free volume theory, the rate of diffusion is related to the free volume available in the system. A current version of the free volume theory [Duda et al., 1982 and Vrentas et al., 1985a, 1985b, 1989] is expressed in Equation (1).

$$D_1 = D_{o1}\exp\left\{\frac{-\gamma(\omega_1 V_1^* + \omega_2 \xi V_2^*)}{V_{FH}^{mix}}\right\} \qquad (1)$$

where

$$\frac{V_{HF}^{mix}}{\gamma} = \frac{\omega_1}{\gamma_1}K_{11}(K_{21} - T_{g1} + T) + \frac{\omega_2}{\gamma_2}K_{12}(K_{22} - T_{g2} + T) \qquad (2)$$

In the case of very small solvent concentration (ω_1 -> 0), since $\frac{V_{HF}^{mix}}{\gamma} \rightarrow \frac{1}{\gamma_2}K_{12}(K_{22} - T_{g2} + T)$,

one obtains the following simplified model:

$$D_{12}^o = D_{o1}\exp\left\{\frac{-\gamma\xi V_2^*}{K_{12}(K_{22} - T_{g2} + T)}\right\} \qquad (3)$$

In Equations (1) to (3), D_1 and D_{12}^o are respectively the self-diffusion coefficient of the solvent in the solvent-polymer system and the limiting diffusion coefficient of the solvent in essentially pure polymer. V_1^* and V_2^* are the critical free volume requirements of the solvent (1) and the polymer (2) jumping units. ω_1 and ω_2 are the mass concentration of the solvent and the polymer respectively. γ (γ_1 for solvent, γ_2 for polymer) is a parameter taking into account the overlapping of free volume since the same free space may be available to more than one molecule. ξ is a parameter characterizing the effect of the sizes of solvent and polymer jumping units on diffusion. V_{HF}^{mix} is the hole free volume, per gram of mixture. K_{11}, K_{21}, K_{12}, K_{22} are constants representing the free volume of solvent and polymer respectively. $\frac{\gamma_2 V_2^*}{K_{12}}$ and K_{22} can be obtained from the WLF constants of the pure polymer. Equations (1) and (3) have been quite successful in correlating and, in some cases, predicting the dependence of diffusion coefficients on temperature and concentration.

Although it has been suggested by some investigators [Ju et al., 1981 and Vrentas et al., 1986, 1990] that ξ can be linearly related to the liquid volume at 0 K, $V_1(0)$, our recent study [Guo et al., 1992] for the diffusion of solvents of different structure in rubbers indicated that such linear relation did not hold in general for nonspherical molecules. This is attributed to the fact that $V_1(0)$, like the Van der Waals volume, only represents the volumetric properties of a molecule well, when the molecule is approximately spherical. In real situations, the solvent molecules involved are usually nonspherical and of very different geometries. $V_1(0)$ in these situations is not a characteristic parameter.

We found that the effect of solvent molecular geometry on diffusion rate is represented by an effective molecular diameter d_{eff}. Based on our experimental data, d_{eff} is found to be a weighted function of the three major dimensions of a molecule, d_{min}, d_{mid} and d_{max} as given in the following relation:

$$d_{eff} = 0.6d_{min} + 0.3d_{mid} + 0.1d_{max} \tag{4}$$

An effective molecular volume V_{eff} is then calculated by using d_{eff} as the diameter of an effective sphere. In Figures 1 and 2, the relations between ξ and V_{eff} and between D_{o1} and V_{eff} for the diffusion of six solvents; methylene chloride, chloroform, carbon tetrachloride, benzene, p-xylene and o-xylene in a natural rubber film are illustrated.

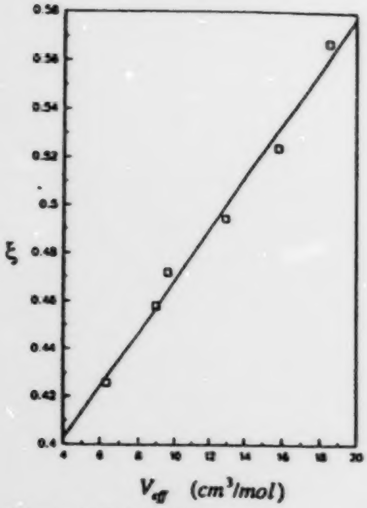

Figure 1. Relation between ξ and V_{eff} for the diffusion of six solvents, methylene chloride, chloroform, carbon tetrachloride, benzene, p-xylene and o-xylene in a natural rubber film.

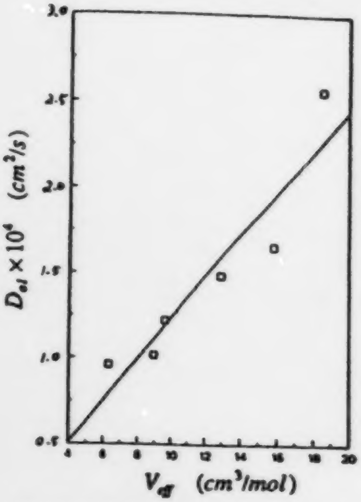

Figure 2. Relation between D_{o1} and V_{eff} for the diffusion of six solvents, methylene chloride, chloroform, carbon tetrachloride, benzene, p-xylene and o-xylene in a natural rubber film.

It is evident from these results that in general the effect of molecular structure on diffusion rate of a solvent in a polymer is much better represented by V_{eff} instead of $V_1(0)$. Since V_{eff} can be directly calculated from the bond lengths and bond angles of a solvent molecule, a reasonable value of ξ can be obtained from the solvent molecular structure. Thus with the WLF constants of the pure polymer available [Ferry, 1970], the diffusion coefficient of a solvent-polymer system can be predicted using Equation (3).

The following is a summary of the simple procedure for the prediction of the diffusion coefficient from polymer physical properties and solvent molecular structure.

-Obtain the glass transition temperature T_{g2} and the WLF constants of the pure polymer.

-Calculate V_{eff} of the solvent molecule using its bond length and bond angle information.

-Use the calculated V_{eff} to estimate the value of ξ and D_{o1} for the solvent in the polymer.

-Predict D_{12}° using equation (3). The mutual diffusion coefficient of a polymer-solvent system can be related to D_{12}° and to the solvent concentration through the free volume model. The breakthrough time of a solvent penetrating a polymeric film can be calculated by solving the diffusion equation with a concentration-dependent diffusion coefficient numerically over the thickness of the film.

The advantage of this approach is that one can estimate the permeation rate of a hazardous solvent through a given polymer without actually experimentally testing the solvent-polymer system. What is needed is to measure a few points for the diffusion of a relatively nonhazardous solvent in the required polymer, in order to determine the relation between ξ, D_{o1} and the solvent molecular structure. For instance, we recommend the use of n-hexane and chloroform as the testing solvents since they have relatively faster diffusion rate and are less toxic. Once the dependence of ξ and D_{o1} on solvent molecular geometry is quantified for a given polymeric material, one can obtain reliable estimation of the permeation rate of a number of other solvents of known structure in a given polymer film.

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Pre-Incident Activities for Hazardous Substances

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1.0 INTRODUCTION

Hazardous substances contribute to the standard of living that we enjoy today. They are used to produce synthetic fabrics, plastics, paper products, and many other consumer products we find in our homes and offices. Other hazardous substances power our vehicles, waterproof our clothes and purify our drinking water.

As a result of our increased usage of hazardous substances, more and more of them are used, stored or pass through our communities. Today there are more than 100,000 commercial hazardous substances available throughout the world. Of these over 30,000 are found in Canada, with new substances being added to this inventory each year.

The vast majority of these substances are manufactured, transported and used safely. On the other hand, there are approximately 15,000 chemical and oil spills in Canada each year. This translates into an average of 40 incidents per day. Most of these incidents are small and are handled quickly with no risk to the public. Unfortunately .025% of the incidents are classified as a major incident and require a major response effort. Many of these incidents include the evacuation of the public. These major emergencies generally occur without warning and will disrupt the daily activities of the community. What can the community do to prevent or reduce the impact from a hazardous substance emergency? One answer is to be prepared. This is achieved through prevention and preparedness measures that are in line with the risk presented and the community resources available.

2.0 RISK

Risk is a measure of the probability and severity of an adverse effect to health, property, or the environment. Risk is often estimated by the mathematical expectation of the consequence of an adverse event occurring (i.e., the product of "probability x consequence"). However, a more general interpretation of risk involves probability and consequences in a non product (mathematical) form. This presentation is sometimes useful in that a spectrum of consequences, with each magnitude having its own corresponding probability of occurrence, is outlined.[1]

Individual risk is defined as the probability in any year of an individual being killed or injured. The probability may be expressed as the "odds" (chance) of it happening. For example, a person in Canada between the ages of 35 to 40, has an annual individual risk of death from all causes of about 1 in 1000 (this may also be expressed as 10^{-3}).

The following is general practice in relation to risks:

$<10^{-4}$	Unacceptable
10^{-5}	Requires Careful Consideration - Limited Access
$>10^{-6}$	Acceptable

The society risk can be described as the average number of persons inside the fatality curve.

3.0 THE RISK MANAGEMENT OF HAZARDOUS SUBSTANCES

What is risk management? Risk management is the complete process of risk assessment and risk control. Whose responsibility is it to implement a risk management program for hazardous substance safety? It is the responsibility of the manufacturer, supplier, transporter, user and the government to ensure worker and public safety.

The remainder of this paper will look at activities that the municipal government will be implementing to manage hazardous substances. Hazardous substances can be found in, or passing through every community.

Even though we are looking at municipal government activities, it must be recognized that there must be a strong working partnership between government and industry to maximize activities leading to enhanced hazardous materials safety.

3.1 THE MUNICIPALITY

The municipality plays a major role in making the community a safe place to live. In relation to hazardous substances, the municipality must be prepared to reduce the likelihood of an incident and be prepared to respond to those incidents that may occur. This requires pre-planning and developing a response capability bases upon proven risk management techniques. In developing and maintaining a risk management program, the municipality will be guided by their risk management committee.

The typical municipal risk management committee will consist of persons representing: an elected office, the local disaster service agency, each of the emergency services, persons with knowledge about hazardous substances (industry, provincial government, etc.) and the transportation industry. Other representation may be considered based upon the needs of the individual community.

The municipality is also responsible for the development and maintenance of the municipal emergency plan. After risk reduction activities have been completed, the municipality must update and maintain its emergency plan. Again this will require the input and assistance from local industry.

3.2 RISK ASSESSMENT

Risk assessment involves hazard identification and estimating and evaluating the risk that may result in the event of an incident. The risk assessment phase will naturally lead to consideration of possible risk control measures and their effect in reducing the identified risks.

3.2.1 Hazard Identification

At the municipal level, the hazard identification will be based upon finding those locations where hazardous substances are found in quantities that pose a risk to the public. For existing sites (manufacturers, distributors, warehouses, terminals, etc.) that produce, handle or store quantities of hazardous substances, it will become the task of the fire services and/or the local director of disaster services to visit these locations to collect the necessary data. Information gathering for transportation corridors (road, rail, etc.) may be gathered by other departments (e.g., transportation, public works, railroads, etc.) and forwarded to the committee.

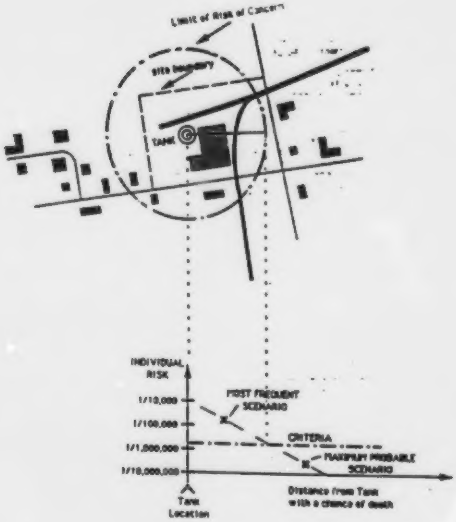
3.2.2 Risk Analysis

Once the data has been collected, a quantitative risk assessment will be carried out. This evaluation (in numerical terms) includes the likelihood of undesired events and the damage being caused together with the significance of the results. The municipality will be using the "Risk Assessment Guidelines for Municipalities" developed by the Major Industrial Accident Council of Canada. By using the "guidelines" the average damage distances and areas will be determined based upon the scenarios selected for the substance identified. These would include the areas where there would be a high risk to life and the area where there is a high risk to health of persons.

The estimate of risk involves the estimate of two dimensions, probability and consequences. The consequences are described by areas where people will be at risk of being killed or injured giving the release of a hazardous substance described by the scenario being evaluated (e.g., BLEVE, gas cloud explosion - instantaneous release, gas cloud explosion - continuous release).

Risk scenarios consists of two possibilities for each quantity of hazardous substance on a site or transportation right-of-way. The first is the "most frequent" release represents all releases that are a small quantity of material but happen relatively frequently. They generally result from the over filling of tanks, improperly closed valves, piping failures, etc. The quantity is very small in relation to the total quantity in the system or container. Typical frequencies are in the 1 in 10 to 1 in 100 year range. The second possibility is for the "maximum probable" release, or a "catastrophic" incident. This would be the total quantity of the hazardous substance in one system and/or container becoming involved in an event. By sticking to these two risk scenario possibilities, risk analysis can be kept as simple as possible while still being realistic.

The risk analysis results in predicted probabilities of the scenario events and their consequences. The consequences are given as individual risk contours for each event for fatalities and for injuries. By transferring the contour lines, to scale, on a map of the area, it is easier to visualize the results of the risk analysis. It is best to use a map that includes all the resident dwellings and other facilities found in the community.

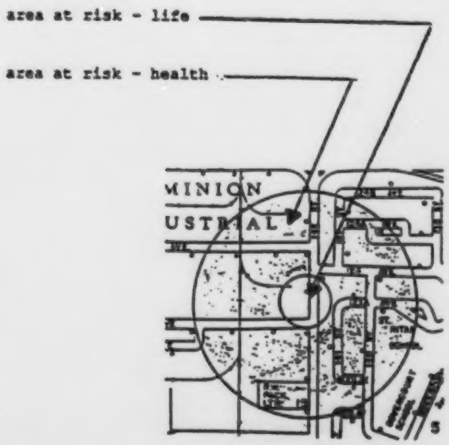

Limit of Risk of Concern
site boundary
TANK
INDIVIDUAL RISK
1/10,000
1/100,000
1/1,000,000
1/10,000,000
MOST FREQUENT SCENARIO
CRITERIA
MAXIMUM PROBABLE SCENARIO
Tank Location
Distance from Tank with a chance of death

Major Concepts in Risk Analysis

3.2.3 Risk Evaluation

Once the risk analysis has been completed and the risk contours line are overlaid on a map risk evaluation can be addressed. The evaluation will show if there is a risk of concern (an unacceptable risk) that will require risk control measures.

When evaluating an entire community, the risks can be listed in order of priority and the resources available can be utilized in the most efficient manner. Under resource limitations, it will become evident which risks are tolerable and which risks require further analysis and their control.


area at risk - life
area at risk - health
MINION
USTRIAL

The graph of probability of individual risk versus distance shown is the fundamental risk estimate that is the measure of the extent of the risk. It will also suggest the magnitude of the response that would be required if the event should occur.

We do not live in a risk free world and we do not have the resources to control all risk. This is why we carry out quantitative risk analysis to ensure the maximum benefits are obtained from the resources devoted to risk control activities.

3.3 RISK CONTROL

An important part of risk management is the implementation of risk control measures where required. Risk control activities result in risk reduction. The result of the reduction achieved can be measure by conducting a new risk analysis now considering the risk control action being considered. In this manner the most appropriate risk control measure can be adopted (so to speak, "getting the most bang for the bucks").

Risk control measures being considered for a complex industrial site will require a more detailed analysis than that outlined in the document.

From the municipal point of view, the major risk control measure is the identification of a risk of concern and the identification of potential actions to reduce or eliminate the risk.

3.4 MUNICIPAL RISK CONTROL

The approach to hazardous substances risk management varies from one municipality to another. Some municipalities are fairly well advanced in the process while others are just beginning. Let us look at some risk control measures that are available to the municipality.

3.4.1 Emergency Planning

In this area most municipalities do well. The municipal emergency plan is an all hazards approach to emergency response. The working together of the municipal government and local industry has benefited many communities. In many communities the industrial emergency plans are attached to the municipal emergency plan as annexes. In many communities the emergency services from the municipality and local industry, plan and train together. Municipal/industrial mutual aid agreements make the community safer due to enhanced resources such as more trained manpower, more equipment and expertise. Three examples in the Edmonton area are: Fort Saskatchewan's Mutual Assistance Program; Strathcona District Mutual Assistance Program; and the Sturgeon Mutual Assistance Program.

3.4.2 Dangerous Goods Routes

As you drive along our highways you may have noticed some signs that contain a black diamond within a green circle. These signs are indicators of a designated dangerous goods route as chosen by the municipality. These routes were selected so there would be minimal risk to the public from those vehicles transporting dangerous goods.

Local authorities are given the power to restrict the traffic of dangerous goods within their jurisdiction under section 17 of Alberta's Transportation of Dangerous Goods Control Act.

Today there are 24 municipalities that have implemented dangerous goods routes.

3.4.3 Land Use Planning

There are two aspects of land use planning: new development and use of existing sites and facilities.

There is the opportunity to consider the risk factors when developing new industrial sites that are to produce, use, handle or store hazardous substances. Based on the results of the risk assessment, compatible facilities can be located in the same industrial area, with planned access to and from the site and the establishment of buffer zones.

For existing sites and facilities the issues can become complex. Especially if there has been residential or other high risk encroachment of the buffer zone. If this is the case, there must be more effort spent in risk control activities. Risk control activities may include risk communication, risk reduction, public warning systems, response planning and capability, etc.

Another option available to the municipality is the requirement of a risk assessment for hazardous substance location. Based upon the finding of the risk assessment the municipality may or may not issue a business licence.

Further to municipal planning and development would be zoning requirement to control the development of residences, schools, high rises, shopping centres, transportation corridors, etc.

3.4.4 Training

The subject of training is necessary for all aspects of a risk management of hazardous substances. Training programs must be made available to support the risk management program. Persons from the municipality that may wish to participate in this training include: elected officials, emergency planners, emergency responders, land use planners, transportation planners, economic development officials, business licencing staff, etc. Key points of the training would focus on:

- understanding the importance of developing and maintaining risk management program;
- providing the necessary resources to support the program;

- clearly define what risks are deemed to be acceptable from those that are not;
- to be able to assess the current state of the community and to implement risk control measures where required;
- solicit the cooperation of industry and benefit from their expertise;
- ensure risk control methods in place are well documented and that they are not compromised;
- for existing risks set priorities for those risk control measures required so that municipal and industrial/commercial resources can be maximized;
- formalize cooperative (municipal/industrial) emergency planning and emergency response assistance agreements;
- develop procedures, based upon risk assessment for the issuance of business licenses and transportation routes; and
- develop and maintain programs that will guide the municipality in future development of the community through land use planning.

4.0 PREVENTION VS PREPAREDNESS

Efforts spent on prevention measures should receive priority when possible. Prevention measures are designed to lessen the frequency and impact of a incident upon the public and the environment before an event occurs. Examples may include site location, operating procedures, quantities stored on site, transportation routing, etc.

Preparedness measures recognize an emergency will happen and the focus shifts to reducing the impact on the public and the environment as a result of an incident. This area deals more to the actual response and mitigation of the incident. Efforts are also required in this area but it is best to devote a major portion of the resources available to eliminate or to greatly reduce the likelihood of the incident. Examples of preparedness activities include: emergency planning, public warning systems, response training, mutual assistance agreements, etc.

5.0 CONCLUSIONS

The municipal and public awareness has increased dramatically concerning the safety of hazardous substances over the last decade. This has resulted in the generation of new legislation throughout the world in response to the complex issues facing the manufacturing, transporting, use and disposal of these materials. It is only a matter of time before we see many new initiatives by industry and the government that will result in the improved safety when dealing with hazardous substances.

Footnote

1. "Risk" definition obtained from CSA-Q634-91 Standard.

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Major Industrial Accident Council of Canada
Working Group 1 Proceedings
265 Carling Avenue, Suite 600
Ottawa, Ontario K1S 2E1

Hazardous Martials Emergency Planning Guide
NRT - 1
National Response Team
National Oil and Hazardous Substance Contingency Plan
G-WER/12, 2100 2nd Street SW
Washington, D.C. 20593

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A Transportable System of Models for Natural Resource Damage Assessment

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ABSTRACT

A system of computer models has been developed for assessment of natural resource economic damages resulting from spills of oil and hazardous materials in marine and freshwater environments. Under United States Federal legislation, the results of the model system are presumed correct in damage litigation proceedings. The model can address a wide range of spatial and temporal scales. The equations describing the motion of both pollutants and biota are solved in three dimensions. The model can simulate continuous releases of a contaminant, with representation of complex coastal boundaries, variable bathymetry, multiple shoreline types, and spatially variable ecosystem habitats. A graphic user interface (GUI) gives the user facile control of the system, as well as the ability to display elements of the underlying geographical information system (GIS) data base. The model is implemented on a personal microcomputer, and on a UNIX workstation. The system has been developed for lakes, rivers, estuarine and marine environments. The structure of the system is such that transport to new geographic regions can be accomplished relatively easily, requiring only the development of the appropriate physical, toxicological, biological, and economic data sets. Applications are currently in progress for U.S. inland and coastal waters, the Adriatic Sea, the Strait of Sicily, the Gulf of Suez, and the Baltic Sea.

INTRODUCTION

Proliferating environmental problems associated with accidental releases of chemicals, oil, and refined petroleum products prompted enactment of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) in the United States. CERCLA allows the Federal or a state government, as trustee of affected natural resources, to claim compensation for damages to those resources, as well as the reasonable cost of conducting a natural resource damage assessment. The first computer-based methodology for use under CERCLA (Reed et al., 1989) was developed for the U.S. coastal and marine environments. More recent versions are applicable to both freshwater and saltwater environments.

The system is comprised of a series of linked submodels and data bases (Figure 1). The model is supported by a geographical information system (GIS) which supplies spatially distributed environmental and biotic information to the dynamic physical fates and biological submodels.

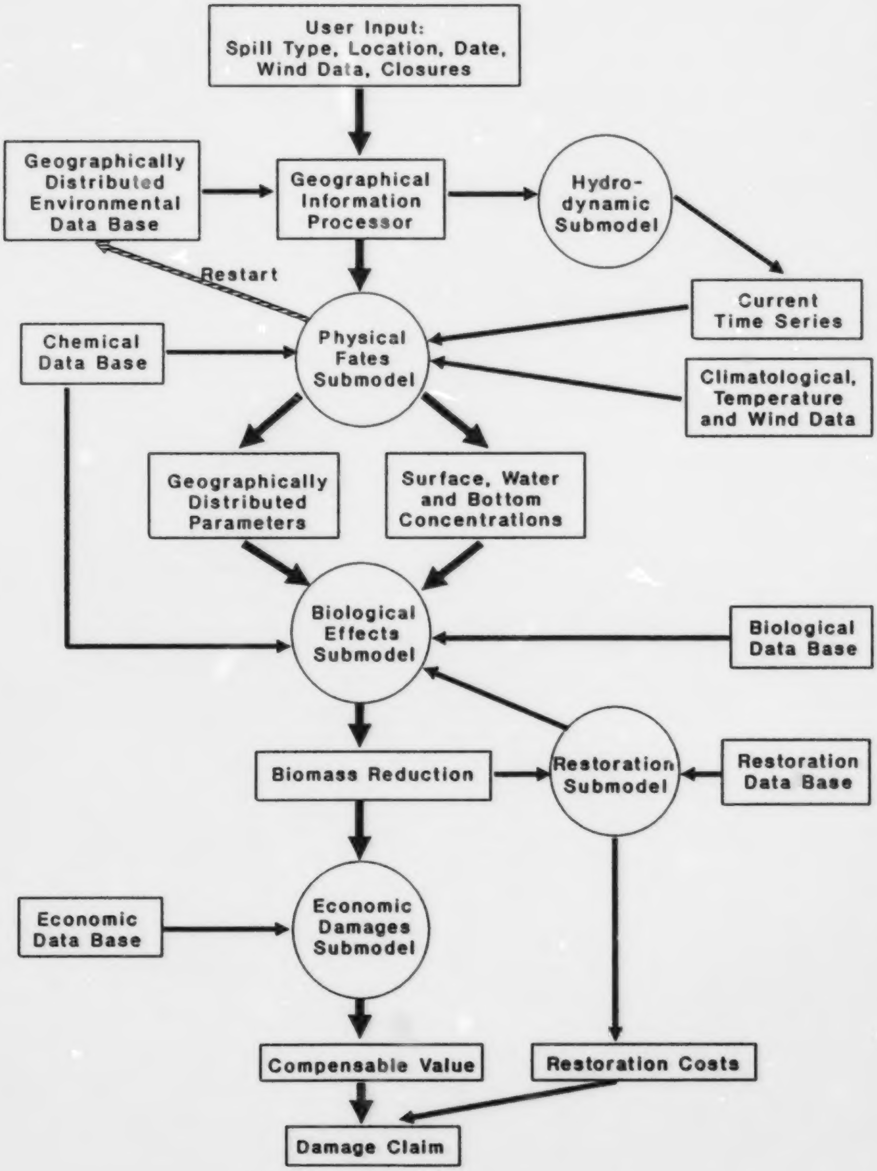
User Input:
Spill Type, Location, Date, Wind Data, Closures
Geographically Distributed Environmental Data Base
Geographical Information Processor
Hydro-dynamic Submodel
Restart
Current Time Series
Chemical Data Base
Physical Fates Submodel
Climatological, Temperature and Wind Data
Geographically Distributed Parameters
Surface, Water and Bottom Concentrations
Biological Effects Submodel
Biological Data Base
Biomass Reduction
Restoration Submodel
Restoration Data Base
Economic Data Base
Economic Damages Submodel
Compensable Value
Restoration Costs
Damage Claim

Figure 1 Schematic overview of the NRDAM/GLE.

The physical fates model computes the dynamic distribution of the spilled substance in the marine or freshwater environment. Computations continue until either (a) all environmental exposure levels are below a minimum threshold, or (b) a surface slick or water column concentration above the threshold is advected outside the model domain. Under case (a) above, control is passed to the biological effects model and computations proceed. If one of the conditions under (b) occurs, the model will restart using a larger grid size or an adjacent downstream grid, so that damages may be computed for the active life of the release.

The biological effects model computes (1) direct lethal effects on larvae, juveniles and adult fish, waterfowl, shorebirds, and lower trophic biota; (2) indirect and long term effects involving the eventual loss of fish as a result of lost larvae and juveniles, and birds as a result of lost broods; (3) indirect effects of lost lower trophic biota and non-commercial species through the food web. These effects are computed by dynamic juxtaposition of biotic distributions with the distributions of the spilled substance on the water surface, in the water column, in the sediments, and along the shoreline.

The economic submodel then proceeds to compute damages based on consumptive use (fishing, hunting, trapping), non-consumptive use (viewing) and non-use (existence) values. The costs of restoration are also computed. All damages are then summed to produce a final damage measure in U.S. dollars for the release.

PHYSICAL FATES SUBMODEL

The purpose of the physical fates submodel is to estimate the distribution of a contaminant on the water surface, concentrations in the water column, and in the sediments. The GIS supplies parameter values for depth, sediment type, ecological habitat, shoreline type, and ice cover throughout the established domain. The chemical data base supplies chemical parameters required by the submodel. The user is required to supply a wind time series specific to the time and location of the spill. The GIS supplies climatological values for air and water temperatures; these may be overridden by the user.

If the specific gravity of a spilled chemical is less than or equal to that of water, the model employs surface spreading, advection, entrainment, and volatilization algorithms to determine transport and fate at the surface. A contaminant with specific gravity greater than water is modeled by a convective jet algorithm which allows the contaminant plume to reach an equilibrium position in a stratified water column, or to sink to the bottom. In general, some fraction of any contaminant spilled will exist in both the water column and the sediments. In the water column, horizontal and vertical advection and dispersion are simulated by random walk procedures. Partitioning between the particulate adsorbed and dissolved states is calculated based on linear equilibrium theory. The contaminant fraction that is adsorbed to suspended particulate matter is assumed to settle at a rate typical for the lacustrine environment. Contaminants at the bottom are mixed into the underlying sediments according to a simple bioturbation equation.

The physical environment is divided into six general compartments: the atmosphere, the sea surface, the upper and lower water column (as defined by the presence of a thermocline), the lake bottom, and the shoreline. The model distributes a contaminant dynamically within and among these compartments. Only the atmospheric compartment has no physical representation and no linkage to the biological effects submodel.

The model solves the generalized transport equations

$$\frac{\delta C}{\delta t} + \vec{V} \cdot \vec{\nabla} C = \vec{\nabla} \cdot D\vec{\nabla} - \sum_{j=1}^{n} r_j C.$$

On the water surface and the shoreline, concentration C has units of mass per unit area, whereas in the water column the units are mass per unit volume. The terms r_j are process rates, including

- evaporation from surface slicks,
- spreading of surface slicks,
- deposition from water surface onto coastline,
- entrainment and dissolution into the water column,
- volatilization from water column,
- degradation (surface, water column, shoreline, sediments),
- mass removal by cleanup,
- addition of mass from continuous release,
- dissolution from sediments to water column,
- deposition from water column to sediments.
- removal from coastline to water column.

These process rates result in mass transfers from one model compartment to another.

An Eulerian (fixed) grid system is established by the software for each application of the model. The grid systems are selected based on the need to resolve the geometry of the area, the availability of natural resource information, and best available estimates of transport velocities. The grid systems have been selected based on the need to resolve the geometry of the rivers, and the availability of natural resource information along the rivers. Grid cell sizes typically range from a few hundred to a few thousand meters.

The use of Lagrangian particles in the contaminant transport calculations simplifies the problems associated with mass transfer from one grid to the next. The governing characteristics of a particle (mass, latitude, longitude, depth, and time since release) are written to a temporary file when a particle exits a grid into another grid. When all damages have ceased in the first grid, then the simulation continues in the subsequent grid, with mass particles being entered into the new grid at the appropriate locations and times, read from the temporary file.

A second expanding, translating ("floating" or Lagrangian) 3-dimensional grid system is used to resolve concentration levels in the water column. At each timestep for which water column concentrations are to be output to the biological submodel, the Lagrangian grid is "stretched" in the vertical and horizontal dimensions until all contaminant particles are within the grid boundaries, at which time concentrations are computed within each three dimensional grid cell. This expanding grid allows the model to adjust to a wide range of spill sizes, and reduces the interdependence between the dimensions of the Eulerian (fixed) transport grid and the size of the spill.

GEOGRAPHIC INFORMATION SYSTEM AND DATA BASE

A geographical information system (GIS) and data base are built into the model system. Once the model grid system has been selected, the GIS fills model arrays with necessary variables and parameters. Depending on whether the model grid cells are larger or smaller than the resolution of the source data, averaging or interpolation is performed to fill each cell in each model array.

Transport currents in the model are of several types: wind-driven currents in lakes, and pressure gradient currents in the connecting channels. Tidal currents are also included in marine areas.

The user is required to supply a wind time series (data set) for each application of the model. This data set can be created interactively from within the model, by directly editing an ASCII file external to the system, or by automated processing of a source file (e.g. airport or weather station time series) into the format required by the model. The GIS data base also contains climatological winds, which are used when the user-supplied wind data set ends.

BIOLOGICAL EFFECTS SUBMODEL

The biological effects submodel estimates short-term losses (injury) resulting from a spill (i.e., losses at the time of the spill and while toxic concentrations remain in the environment) in terms of direct mortality and biomass not produced because of the loss of food resources. Losses are estimated by species or species group for fish and wildlife (birds and mammals).

The environment is represented by grids of habitats with each grid cell coded as to habitat type. A grouping of habitat grid cells with the same habitat code constitutes an ecosystem in the biological submodel. Fish, birds, mammals and rates of lower trophic level productivity are assumed constant and evenly distributed across an ecosystem within each of four seasons. Fish, birds and mammals are assumed to move at random within each ecosystem during a single season. Fish eggs and larvae are assumed constant and evenly distributed across each ecosystem within each month of an annual cycle. Planktonic stages are advected with the currents.

Habitats include deepwater, nearshore, and wetland environments. Habitat types are defined by depth, proximity to shoreline(s), bottom type, and dominant vegetation type. The water column may be a single layer or divided into two layers by a thermocline.

The physical fates submodel calculates concentration in three-dimensional space and in time. This information is passed to the biological effects submodel where the portion of exposed organisms in each habitat type which would be killed is calculated from dissolved concentration (in the water or sediment). Mortality is calculated using laboratory acute toxicity test data (LC50, concentration lethal to 50% of test individuals) corrected for temperature and time of exposure, and assuming a log-normal relationship between percent mortality and dissolved concentration. Organisms killed are integrated over space and time and by habitat type to calculate a total short- term kill. This total short-term kill occurs from the time of the spill until the time the contaminant is dispersed to the point where concentrations are below toxic levels.

Biomass which is not produced as a result of a loss of food resources is estimated using a simple food web model. Lost primary (plant) and secondary (herbivore) production in each habitat is estimated using the EC50, the concentration where growth rate is 50% of the clean control, correcting it for temperature and assuming a log-normal relationship between percent of uninhibited growth rate and concentration. Primary and secondary production losses are integrated over space and time and by habitat to calculate the total weight not produced during the spill. The rates of production are assumed to return to normal immediately following the dispersion of the spill to non-toxic concentrations. The portion of the lost primary production which would have produced primary consumer (secondary producer or herbivore) biomass is estimated based on observations ecological efficiency made on representative ecosystems. The fractions of the lost secondary production which would have been consumed by each of their predators (fish, birds and mammals) are assumed to be proportional to the biomass of that predator relative to the sum of its competitors. The output of this part of the submodel is lost production of the various fish, bird and mammal species or species categories as a result of the spill. This is added to the total direct kill to yield a total loss of biomass by habitat as a short-term result of the spill.

Potential long-term losses (losses seen after the spill has dissipated) which can result from a spill of a toxic substance include: (1) lost recruitment to a fishery of the larvae and juveniles killed at the time of the spill; (2) lost future growth of the adults killed at the time of the spill; (3) changes in food web structure and, therefore, productivity of specific trophic levels and populations; and (4) chronic effects of sublethal levels of contaminants in tissues or the environment, such as reduced growth rate or loss of reproductive potential. The latter two effects are considered beyond the scope of this model, both due to the complexity of developing such models, which necessitates that they be site-specific, and to the lack of quantitative information required to run these models. Thus, the impacts estimated in the biological submodel are the results of acute toxicity and resulting direct effects on long-term productivity and yield: lost recruitment and lost growth. It is assumed that the spill has no indirect (chronic) effects or feedbacks after the spill has dissipated, such as changes in mortality due to density-dependent effects, changes in food web structure and predator-prey relationships, or changes in reproductive potential. The spill impact extends only for the life span of the species considered, and growth, biomass and reproduction are assumed to return to normal immediately after the effects of the spill have dissipated.

For fish, it is assumed that a constant mortality rate (due to natural causes) applies to juveniles and adults of a species, juveniles and adults inhabit the same habitat at the same time, there is a constant fishing mortality rate on adults, there is a constant larval survival rate, and the growth rate for adults past the age of recruitment to the fishery follows the von Bertalanffy relationship. Using these assumptions and standard steady-state fisheries models, the age structure of a population and long-term losses in yield as the result of the spill may be estimated. The initial kill in numbers by age is calculated from fish biomass killed, weight as a function of age, and natural and fishing mortality rates. For each year following the spill, the lost catch, calculated from fishing mortality, weight by age and average number alive during that year, is passed to the economic damages submodel. Thus, only those individuals which would have been caught in present and future years, and not those which would have died naturally, are included in the quantification of the effects of the incident.

The relatively high mortality rates of fish larvae are included in the biological effects submodel, since a high number of the larvae killed at the time of the spill would have died regardless of the spill. Larvae and older age classes are not assumed to be inhabiting the same environment concurrently, and their losses are calculated separately.

For waterfowl and mammals, losses to hunting are calculated assuming constant natural and hunting mortality rates over time after the spill. For all wildlife, losses to viewing are calculated as the number not left alive in present and future years as the result of the spill, after constant natural mortality (and hunting mortality) is subtracted.

Lost catch (or lost number hunted) as the result of area closures to fishing or hunting is also calculated in the biological effects submodel for each species or species group. Catch lost due to closure, but not due to mortality, is added to mortality-induced catch losses to calculate total lost catch. Total lost catch by season, year and habitat type is output to the economic damages submodel where monetary damages are calculated.

The biological effects submodel was designed to be generally applicable, while restricting the data and parameter requirements to information which is readily available. Thus, biological data are compiled for a series of habitat types within each region, as opposed to specific information for each possible geographic location.

Data contained in the biological data base are seasonal estimates of fish biomass per area (kg wet weight per km^2), numbers of birds and mammals per area, and rates of production for lower trophic levels (plants and invertebrates).

Parameters required for the biological submodel include estimates of natural and fishing (hunting) mortality rates, available from the fisheries and wildlife literature; age-specific growth rates, available from length- or weight-at-age catch data; and age at recruitment and life span. The spawning areas and times for fish species, and development information for the young of all species groups are also required. All of these parameters are included in the data base as specific to habitat within each geographic region.

ECONOMIC DAMAGES SUBMODEL

The economic damages submodel calculates damage to both commercial and recreational fisheries. The quantity of fish which would have been harvested in the absence of the incident is an output of the biological effects submodel. The value of the reduction in harvest or other use minus the cost of harvesting or using the resources is the lost in-situ use value of the resource. This provides a measure of the damages resulting from the spill.

Damages resulting from injury to lower trophic-level, non-commercial organisms are based on the ultimate loss in the in-situ use value of predator species (commercial and recreational fisheries, birds, and mammals) which occurs when an incident affects the productivity of the food web. The food web model developed in the biological effects submodel quantifies the biological injuries which arise over time as a result of the incident. Economic damages are measured using the concepts and data applicable to commercial and recreational fisheries and wildlife (birds, mammals, reptiles).

Injury to wildlife results in losses of consumptive (hunting) and non-consumptive (e.g., viewing, photographing) in-situ use values. The quantification of biological injury to wildlife is an output of the biological effects submodel. Damages resulting from losses in consumptive use are measured using available estimates of the marginal value of an additional animal (e.g., duck or goose) harvest. Damages arising from losses in non-consumptive use value for non-game species are measured by employing an estimate of the marginal change in value associated with a change in the viewable wildlife population.

Damages caused by injury to public beaches are estimated by the lost in- situ use value of a length of beach which depends on the season, the type of public beach affected and the extent and duration of the injury.

RESTORATION SUBMODEL

The model system also includes calculations of the costs of restoration or replacement of natural resources and their services, as well as damages based on lost value of injured resources. The procedure used by the restoration model is summarized as follows:

(1) Quantify injury to natural resources in terms of lost or disrupted services (using the biological effects models).

(2) Determine alternative actions which would restore (or replace) the resources and services in a cost-effective manner.

(3) Include in damages lost services over the time required to accomplish restoration (i.e., consideration is given to the ability of the resource to recover and the value of the lost services through the recovery period).

The restoration submodel determines possible alternative restoration actions, whether those actions are technically feasible (i.e., whether those actions can be performed to reduce injury and thus damages), cost effectiveness of the actions, and what alternative replacement actions for services lost might be performed if direct restoration is not feasible. This determination is made for each of the habitat types affected by the spill.

TACTICAL RESPONSE SUBMODEL

A submodel to simulate strategies for responding to accidental spills has been recently added to the system. Tactical decisions and operational responses to spill events are modeled by manipulation of icons on the computer screen, which shows a map of the study area. Focus is on rapid display of information in a comprehensible form. The user of the system employs a mouse and menu selections to query spill response unit icons and to create schedules for spill response units. An underlying data base maintains information about the response unit's present location, speed and cleanup potential.

For a spill response, the tactical response submodel allows the spill manager to create spill response action sequences for each of the spill response units, to show a predicted time of arrival for each ship track, and to "play back" the spill response showing all of the vessel tracks at once. Mechanical cleanup devices are positioned near surface oil locations and initiate oil skimming simulations in parallel with trajectory simulation. Other response actions, such as burning and dispersant application, may also be simulated.

The tactical response submodel couples to the oil spill fates submodel on tactical approach and operational units used to combat the spill. Spill response units which are available for deployment are simulated to move at their design speeds to locations selected by the spill response supervisor. The fates submodel contains routines which simulate spill response effectiveness of each response unit. Simulations of decreased boom containment and skimmer effectiveness are a function of user-input, time-varying winds. Complex combinations of response unit deployments are stored as response scenarios and can be invoked under the spill response scenario name.

DISCUSSION

The model system is implemented on an IBM/PC 386 computer, with VGA color monitor. A UNIX workstation version is also available. A user-friendly menu system (both keyboard and mouse driven) allows the user to view and enter data, run the model, and view model output. Geographical data and model output are mapped and animated on the color screen and may be printed. Tabular information may be scanned. Data input is by entry into pull-up forms or is mouse driven for graphical information. Locations of site-specific information (such as critical habitats or response equipment) are indicated by colored dots or icons on a map. This information may be interrogated and updated by the user using a windowing system into a textual data base.

The model may be used to quantify physical fates, biological impacts and economic damages resulting from release of pollutants into aquatic environments for many purposes. Natural resource damage assessments under U.S. Federal regulations represent just one example application. The relative impacts of various spills may be used to focus response efforts. Maximum liabilities for accidental spills may be estimated, and the results of various management strategies may be investigated.

The model system has seen a variety of applications, including natural resource damage assessments for actual spills (French, 1990). A tactical oil spill model, which allows oil spill response to be managed with consideration of impacts, was developed for Alyeska Pipeline Company (Anderson et al., 1990). Maximum liabilities for harbor and at-sea spills of hazardous substances slated for incineration have also been assessed with this model system (French et al., 1987).

The system of linked computer models discussed here has evolved from an earlier system originally designed for U.S. coastal waters (Reed et al., 1989). The newer version, complete with color graphics and GIS capabilities, has been fully implemented for the U.S. Great Lakes and connecting rivers. The Great Lakes version is expected to be available for public review in autumn, 1992. A version covering the entire coastal United States, including Alaska, Hawaii, and U.S. territories, is scheduled to be available for public review in January, 1993. Applications are also underway in the Mediteranean Sea (Figure 2), the Gulf of Suez, and the Baltic. Thus the system is readily transportable to new regions, and is applicable for arctic, temperate, and tropical climates.

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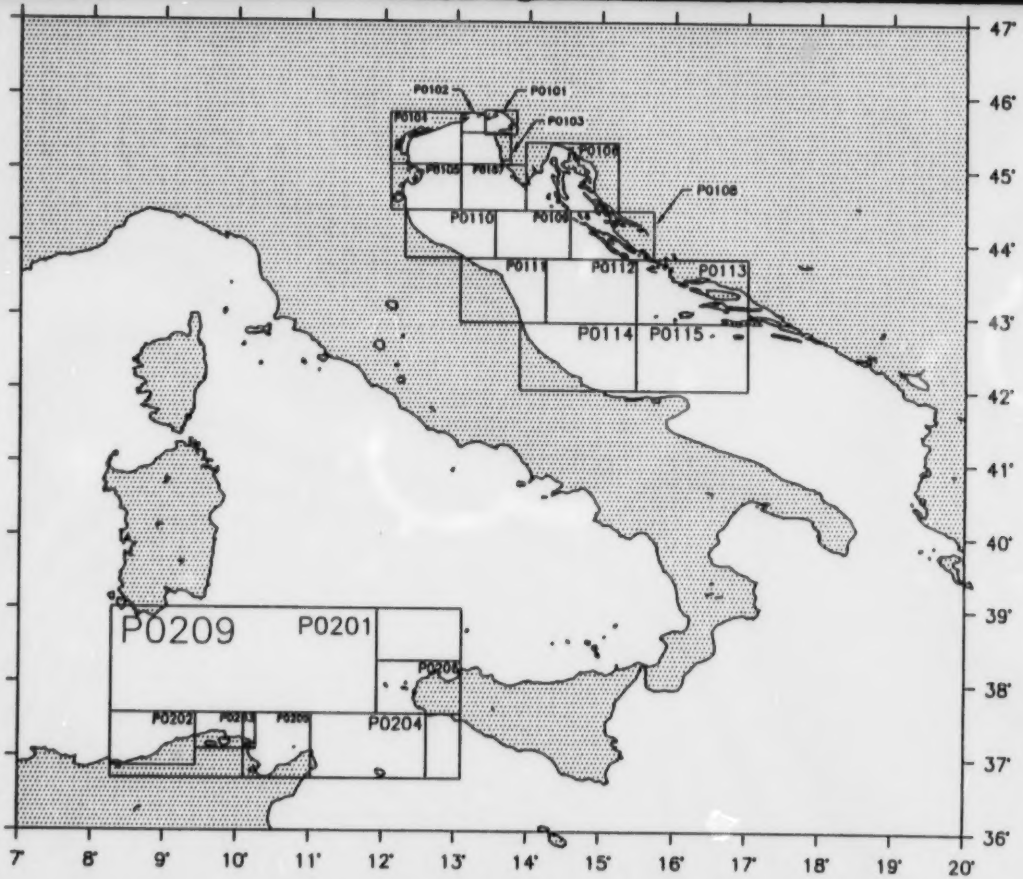
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20°

Figure 2. NRDAM grid systems for the Adriatic and Strait of Sicily applications.

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Risk Assessment of Natural Gas Liquids Pipelines

by

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ABSTRACT

Ethane, propane, butane and pentanes are commonly transported as a liquid in pipelines. These compounds have a high vapour pressure, and when accidentally released, a flammable, heavier-than-air cloud forms. If the cloud is ignited, a fireball, flash fire or vapour cloud explosion may occur. Pipelines are routed to avoid densely populated areas. However, new developments may encroach on existing pipelines. Risks to the public can be estimated to determine an adequate setback distance, and to establish an effective emergency response plan.

The methodology for a risk assessment is described. Consequences and frequencies of the selected hazardous incidents are provided. Individual risk levels in rural and urban areas along the pipeline are presented and compared to day-to-day risks of life and risk criteria proposed by the Major Industrial Accident Coordinating Committee.

SECTION 1

INTRODUCTION

This report estimates risk to which the public could be exposed to as a result of a typical natural gas liquids (NGL) pipelines. Risk is used in the context of measurement of frequency of occurrence of an event, and of the magnitude of the consequences of that event. This may be expressed formally by:

Risk = Frequency x Consequence

Concern in this assessment is with structural damage, injuries or deaths that occur as a result of the event.

A number of qualifying adjectives have been used with the word "risk". Voluntary risks are those assumed voluntarily, e.g., mountaineering, smoking, yachting. Involuntary risks are risks that are imposed on an individual or a group of individuals by decisions made elsewhere in society or by natural occurrences, e.g., siting of industrial facilities, violent storms.

Acceptance of risk usually comes from either a conscious decision (as from an inquiry) or by tacit consent of society. Since there is a possibility of failure in any installation and, hence, some degree of risk to exposed persons, there is tacit acceptance of risk by exposed persons. Some of these risks are assumed voluntarily while others are deemed to be imposed.

The potential hazards of pressurized, flammable liquid pipelines are well known. Although efforts are made to reduce risks as much as possible, some level of risk will remain as in any undertaking. The determination of the level of risk, to which the public could be exposed by a pipeline, is important for several reasons:

- To check the safety standard specified in project planning and design as well as the proposed operating procedures used for the facility;
- To assist with emergency response planning by predicting the effect zone;
- To inform the public who either are, or may be, in a zone that could be affected by an accidental release from the installation;
- To compare the estimated level of risk with existing risks encountered and accepted in day-to-day activities;
- To provide a basis of assessment to assist regulatory authorities.

Risk can be reduced by careful routing, quality engineering, good preventive maintenance and well-designed emergency planning. However, risk is still present in spite of any reduction measures.

1.1 DESIGN AND OPERATING CONDITIONS

Natural gas liquids are a mixture of ethane, propane, butane and pentane. These compounds are gases at atmospheric conditions. Under the high pressure in the pipeline, the components are compressed to form a liquid. NGL's are referred to as high vapour pressure (HVP) liquids. NGL is a highly flammable, colourless, and nearly odourless gas at atmospheric conditions. A typical composition of NGL is given in Table 1.

The design pressure of NGL pipelines is about 10 000 kPa (1440 psi); the normal operating pressure range is from 3000 to 7000 kPa. Throughput volumes of the example pipeline is 7000 m^3/day. A 273.1 mm (10") diameter steel pipe with 6.35 mm (0.25") wall thickness with block valves spaed every 15 km, was assumed.

Table 1. Average NGL Composition.

	Mol Fraction %
Ethane	57
Propane	23
Butane	16
Pentane	4
TOTAL	100

HVP pipelines are constructed to meet or exceed all applicable codes and regulations. If a pipeline route crosses agricultural land with a low population density (designated as Zone 1 in the CAN/CSA Z-183-M90 code), it can be designed to meet less stringent design requirements than for more heavily populated areas (designated as Zone 2 in code). The more stringent measures required for pipelines in urban areas include:

- Pipe that has increased wall thickness.
- Pipeline buried with minimum 1.2 m (4 feet) of cover.
- Remote operation block valves must be installed a maximum of every 15 km.

1.3 OBJECTIVES

The objective of this study is to assess the risks to the public associated with a typical NGL pipeline. The risk is estimated and then compared to the risks of everyday life and risk criteria adopted by regulatory agencies. The risk estimates of this report are the incremental risks to which the public would be exposed.

The effects on the public of an accidental release of NGL are assessed in terms of fatalities, injuries and property damage. It is also necessary to quantify how often the hazardous incidents are expected to occur (known as the frequency). Risk is determined by combining the consequence and frequency results.

The methodology used to estimate risk is described in Section 2. Consequence and frequency results are presented in Section 3. Risk estimates are presented and assessed in Section 4.

SECTION 2

METHODOLOGY

A discussion of the methods used in the analysis of risk associated with a pipeline is given in this section. The steps in the analysis, and the types of input data required are shown in Figure 1. The four basic components of the analysis are:

- Identification of hazardous incidents;
- Estimation of consequences of each hazardous incidents;
- Estimation of the frequencies of each hazardous incidents; and
- Determine risk from all hazardous incident.

2.1 IDENTIFICATION OF HAZARDOUS INCIDENTS

Identification of hazardous incidents is undertaken at a level that addresses major threats from the materials handled, to all members of the public who reside near to or who may come into the vicinity of the proposed installations. The selection of hazardous incidents is made on the basis that they are credible and that they can occur with measurable and significant frequency. Three release scenarios have been considered:

- **Full Rupture** where NGL is emitted from two complete cross sections of the pipe (worst possible release);

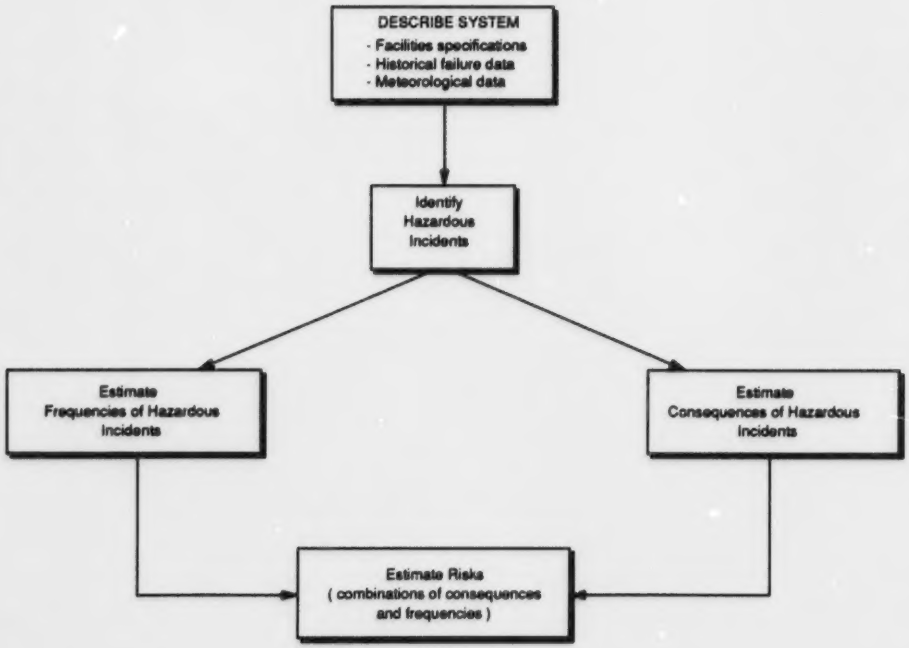
DESCRIBE SYSTEM
- Facilities specifications
- Historical failure data
- Meteorological data
Identify Hazardous Incidents
Estimate Frequencies of Hazardous Incidents
Estimate Consequences of Hazardous Incidents
Estimate Risks (combinations of consequences and frequencies)

Figure 1. Risk analysis methodology (simplified).

- **Partial Rupture** where NGL is emitted from a hole at a flow rate equivalent to the normal expected throughput of the pipeline (worst credible release);

- **Leak** where NGL is emitted from a hole at a flow rate equivalent to 10% of the normal expected throughput of the pipeline (most probable release).

This is a representative set of releases which will result in catastrophic, major and localized incidents, respectively.

The sequence of possible events following a pipeline release is presented in the event tree diagram in Figure 2. The hazardous incidents associated with a release are:

- **Fireball**, if the released material is ignited immediately after the release. A fireball is a burning cloud with a sperical shape. The outer layer of the fireball is a flammable mixture and the inner core is almost pure NGL vapour.

- **Jet fire** following ignition of high pressure vapour and/or liquid releases which entrain air, creating a flammable mixture.

- **Flash Fire** or **Vapour Cloud Explosion**, if ignition takes place away from the source. When NGL is released and immediate ignition does not occur, its mixture with air will form a flammable vapour cloud. A flash fire travels from the point of ignition through the cloud of flammable vapour. Under certain conditions, the flame speed may reach high velocities and produce pressure waves, resulting in a vapour cloud explosion. These events could result in a jet fire when the fire burns back to the release point.

- **No Ignition**, cloud disperses with no consequences to the public, except for the possibility of asphyxiation near the release point.

2.2 CONSEQUENCES OF HAZARDOUS INCIDENTS

Estimating the consequences of hazardous incidents requires the determination of the area around an accident site where the concentration of unignited vapours, thermal radiation or blast waves may have harmful effects on people and property. Mathematical models are used to estimate the size of the hazard zones by determining the intensity of the effect (concentration, thermal radiation, or overpressure) as a function of distance from the source. The models require as input the released material flow rate and properties and meteorological conditions.

2.2.1 NGL Release Rates

Releases of NGL from a pipeline are modelled to determine the flow rate and fluid properties during the blowdown. The initial portion of the release will be as a liquid until the pressure in the pipeline drops to the mixture vapour pressure of 1500 kPa. The NGL, when reduced in pressure, will change phase from a liquid to a vapour.

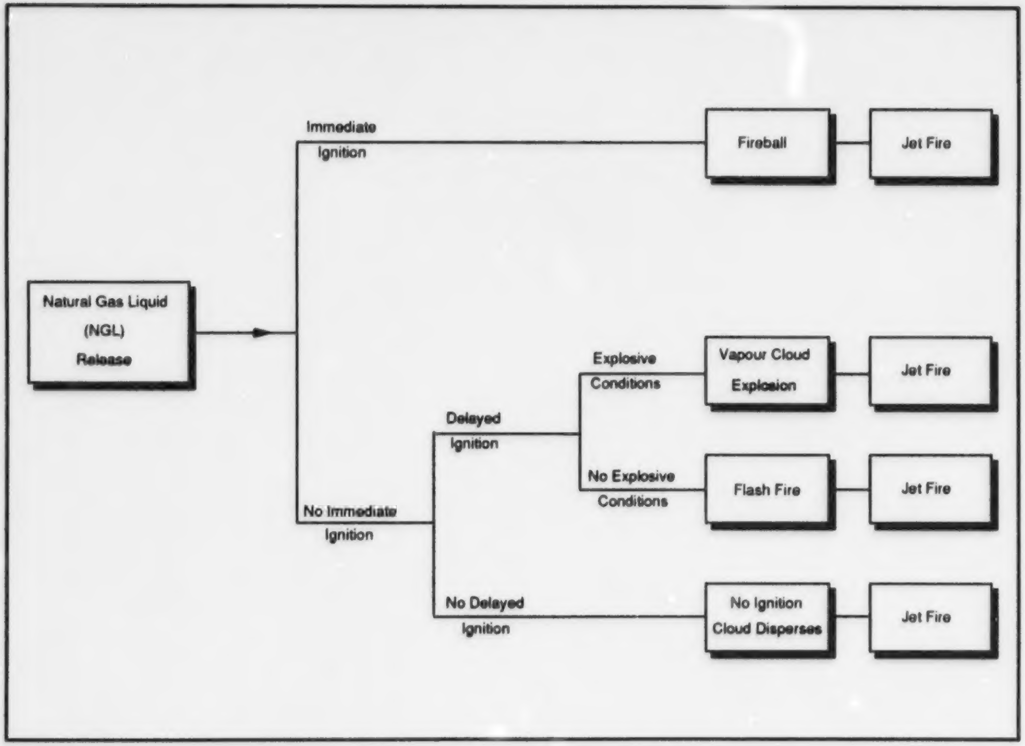
Natural Gas Liquid
(NGL)
Release
Immediate
Ignition
No Immediate
Ignition
Delayed
Ignition
No Delayed
Ignition
Explosive
Conditions
No Explosive
Conditions
Fireball
Vapour Cloud
Explosion
Flash Fire
No Ignition
Cloud Disperses
Jet Fire
Jet Fire
Jet Fire
Jet Fire

Figure 2. Event tree showing sequence of possible events following an NGL release.

Upon flashing to atmospheric pressure the released material has a temperature of -67°C and has a vapour mass fraction of 0.71.

A simplified blowdown model was used to account for the two-phase and multi-component nature of the discharge. The pressure in the pipeline will be maintained at the NGL vapour pressure until all of the liquid is vapourized. During this time the two-phase flow rate is relatively constant (Fauske, 1988). The following constant mass flow rate over the time to discharge the section were used:

- **Full Rupture** - The estimated NGL discharge rate from a full rupture is 432 kg/s. At this rate, it would take approximately 15 minutes to blowdown a 15 km section of pipe. Block valves would close within minutes as the pressure in the pipeline drops very quickly.

- **Partial Rupture** - The normal capacity of the NGL pipeline is 7000 m^3/day or 40.1 kg/s. This flow rate as a two-phase mixture requires a rupture diameter of about 112 mm. The block valves would normally close within minutes of sensing a release has occurred. At this rate, it would take about two and a half hours to blowdown a 15 km segment.

- **Leak** - A leak flow rate of 4 kg/s, equivalent to 10% of the normal capacity of the pipeline, was assumed. The hole size is about 10 mm in diameter, based on liquid flow. A typical leak detection system would detect a leak of this magnitude within 15 minutes, and close the block valves. It would take about 1 day to blowdown a 15 km segment through a leak of this diameter.

2.2.2 Meteorological Conditions

In the event of an NGL release, weather conditions determine the direction of the plume and the amount of dilution in the plume as it moves downwind. The direction is determined by the wind at the time of the release. The dilution is determined by the amount of turbulence in the atmosphere.

Atmospheric turbulence can be generated by thermal or mechanical processes. Heating and cooling of the ground by radiation contributes to the generation and suppression of turbulence, respectively. High wind speeds contribute to the generation of mechanical turbulence. Meteorologists frequently use the following classification scheme when evaluating the dilution capacity of the atmosphere.

- **Unstable** Classes A, B and C are primarily associated with daytime heating which produce increased turbulence levels.

- **Neutral** Class D is primarily associated with high wind speed conditions which result in mechanical turbulence.

- **Stable** Classes E and F are associated with night-time cooling conditions which result in suppressed turbulence levels.

The Atmospheric Environment Service maintains a weather observation network across Canada. Data from the Edmonton Namao Airport was used for this example. Meteorological data have been collected at this station since 1955 (Environment Canada, 1983). Table 2 provides the joint wind speed and stability class frequency distribution based on Namao STAR data from 1973 to 1984. For a given release scenario, the resulting cloud size is very sensitive to the prevailing atmospheric turbulence and wind speed. To avoid modelling each release scenario (3) for each combination of wind speed and stability class (18), four conditions were selected to represent the range of weather conditions. The selected conditions are presented in Section 2.3.2.

Table 2. Wind speed and stability class joint frequency distribution (%).[a]

Pasquill Stability Class	Wind Speed (m/s)						
	0-1.5	1.5-3.1	3.1-5.1	5.1-8.2	8.2-10.8	10.8+	Total
A	0.3						0.3
B	2.9	2.1	0.5				5.6
C	2.7	3.5	5.2	0.3			11.7
D	2.8	8.5	19.7	14.8	2.6	0.7	49.1
E		8.9	7.5				16.4
F	9.2	7.7					16.9
Total	17.9	30.7	32.9	15.1	2.6	0.7	100.0

[a] Based on Edmonton Namao Airport STAR data (1973 to 1984).

An ambient temperature of 15°C was assumed for modelling purposes as this results in larger predicted cloud areas. An annual average relative humidity of 71% was used. Mechanical turbulence can be generated by surface roughness features such as vegetation and buildings. A surface roughness scaling height of 100 cm was used. This is representative of flat or rolling terrain covered with obstructions tens of metres in height (e.g., forests, cities).

2.2.3 Dispersion of NGL

SLAB (Ermak, 1990), a dense gas dispersion model developed by the Lawrence Livermore National Laboratory, was used to determine the concentration of NGL in the atmosphere. SLAB was highly rated in a recent comparison of model predictions to observations (Hanna, 1991).

The model simulates the atmospheric dispersion of denser-than-air releases by accounting for air entrainment into, and gravity spreading of, the heavy gas cloud. The effects of NGL droplet evaporation, water droplet formation and ground heating on the cloud are included.

A vertical release from the crater formed by the release was assumed and the initial release height was set at ground level. Concentrations as a function of downwind distance, crosswind distance, elevation above ground and time are predicted by the model. A 10 second concentration averaging time was used to conservatively estimate the flammability range.

2.2.4 Fireballs and Jet Fires

Empirical models are used to estimate the size and duration of fireballs and the length of jet fires (Crocker and Napier, 1988). Fireballs and jet fires were only modelled for calm winds. A stationary spherical cloud resting on the ground was assumed for a fireball. A vertical line source was assumed for the jet fire. The fraction of energy released as thermal radiation was taken as 30%.

The thermal radiation intensity received by a target normal to the source, accounting for the transmissivity of the atmosphere, was determined. The dose a receptor receives was determined from: (exposure time) times (thermal radiation) $^{4/3}$. A receptor is assumed to be exposed to the entire duration of a fireball. For a jet fire, a receptor is assumed to be stationary for five seconds and then flees from the source at a rate of 2.5 m/s. Probit parameters were used to determine the percentage of the population effected (Clay *et al.* 1988). The effects of thermal radiation on people and property are presented in Section 3.

2.2.5 Flash Fires

Output from the dispersion model was used to determine the extent of a flash fire. Combustion of the NGL - air mixture may occur if the concentration of NGL is between the lower flammable limit (LFL) and the upper flammable limit (UFL). For the NGL considered, the LFL concentration is 2.4% NGL on a volume basis in air (24,000 ppmv) and the UFL concentration is 10.9% (109,000 ppmv).

If ignition occurs, a flash fire propagates through the area where the concentration is greater than the LFL. It is conservatively assumed that people and buildings within a flash fire are engulfed in flames and do not survive the exposure (TNO, 1988).

The size of the flammable cloud grows as the release progresses until the maximum size is reached. The maximum size of the cloud was used in the assessment. For the partial rupture and leak, the maximum cloud forms early in the release and is not sensitive to the release duration time. For the full rupture, the size of the cloud decreases with decreasing release duration and shorter pipeline segments would have smaller flammable clouds.

2.2.6 Vapour Cloud Explosions

In certain cases, flash fires propagate so quickly through the flammable mixture that a blast wave is created. The explosive mass of the cloud between the LFL and UFL concentrations was determined by integrating the output of the dispersion model. The centre of mass (epicentre) was also determined. The maximum explosive mass is used in the assessment. The explosive mass of a cloud from a worst possible release decreases with decreasing blowdown length.

The TNT model was used to determine the overpressure as a function of distance with 10% of the heat of combustion of the NGL converted into the production of blast waves. Peak overpressures within the vapour cloud are 100 kPa (AIChE, 1989).

In the event of a vapour cloud explosion, people and structures within the LFL are assumed not to survive (TNO, 1988). The cause of death is direct flame contact and/or asphyxiation through lack of oxygen. The effects of the overpressure on people and property outside of the LFL are presented in Section 3. A probit approach was used to determine the probability of the given effect as a function of distance from the epicentre (Eisenburg 1975, Clay *et al.* 1988).

2.2.7 Asphyxiation

The danger of asphyxiation must be considered at high concentrations of NGL. If the NGL concentration in air exceeds 24% (about twice the UFL), the oxygen concentration is less than 16% in the NGL-air mixture. To be conservative, the UFL will be used as the NGL concentration where people may be temporarily effected by asphyxiation. At 16% oxygen, breathing and pulse rate increases, and muscular coordination is slightly disturbed (Clayton and Clayton, 1982).

2.3 FREQUENCIES OF HAZARDOUS INCIDENTS

The frequency of occurrence of hazardous incidents was estimated from fault and event tree analyses. The frequency of hazardous incidents is a combination of the release frequencies, the probability that the meteorological condition occurs and the probability that ignition occurs.

2.3.1 Release Frequencies

Alberta's Energy Resources Conservation Board (ERCB) maintains a computerized database of HVP pipeline failures in the province of Alberta. Under the Pipelines Act, it is mandatory for pipeline operators to report releases of material of any quantity and the magnitude of consequences. The ERCB has the following definitions for leaks and ruptures:

- A leak is a small opening or crack in the pipeline causing some product loss but not immediately impairing the operation of the line;

- A rupture is the instantaneous tearing or fracturing of the pipe material causing immediate impairment of the operation of the pipeline.

The number of pipeline ruptures and leaks according to the principal causes are presented in Table 3. There were 14 ruptures and 24 leaks from the years 1975 to 1990. Releases that occurred while testing non-operational pipelines are not included. From 1975 to 1990 there was an estimated 75,440 km·yr of HVP pipelines in service.

The historical pipeline frequencies are also presented in Table 3. The frequency of the ruptures is estimated to be 1.9×10^{-4} ruptures/km·yr; this frequency is obtained by dividing the number of ruptures from 1975 to 1990 by the cumulative pipeline length during the same period.

The nine ruptures due to external forces were caused by third parties. A rupture due to third party damage has not occurred since 1985. This is due to increased public awareness programs such as Alberta First Call.

One-ninth of pipeline ruptures are assumed to be full ruptures, based on an analysis of sour gas pipeline ruptures (ERCB, 1990). Similar data does not exist for HVP pipelines. The other eight-ninths of pipeline ruptures are represented by the partial rupture release case.

The frequency of leaks is estimated to be 3.2×10^{-4} leaks/km·yr. Leaks are 1.7 times more likely to occur than ruptures.

2.3.2 Meteorology

Meteorological data from the Edmonton Namao Airport for the 10 year period 1973 to 1984 were evaluated (AES, 1987). Figure 3 provides a summary of the wind direction, wind speed and stability class frequency distribution.

The wind direction frequency distribution is referred to as a "wind rose". The direction of the bar on the wind rose indicates the direction the wind is blowing from. The most frequent winds are from the west (~ 14%) and that the least frequent winds are from the north-northeast (~ 2%). However, in this example a uniform wind rose will be assumed to simplify the calculations.

The average windspeed in the area is 16.7 km/h (4.6 m/s). The wind speed class histogram indicates that wind speeds below 6 km/h occur 18% of the time, the most likely wind speeds are in the 11 to 19 km/h range (33% of the time) and that wind speeds greater than 39 km/h occur 2% of the time. These wind speed measurements refer to those observed at the 10 m level. The dense gas dispersion model accounts for the decrease in windspeed near ground level.

The stability class histogram indicates that the most likely stability category is D (the neutral class) which occurs about one-half the time. For uncontrolled gas releases near the ground, the stable Class F category often becomes the "least favourable" meteorology condition. This class occurs about 17% of the time. Table 4 gives the

Table 3. Release Frequencies from HVP Pipelines in Alberta (1975 - 1990).

Cause	Leaks Number	Leaks Frequency[a] (#/km·yr)	Ruptures Number	Ruptures Frequency[a] (#/km·yr)
Corrosion	5	6.6×10^{-5}	0	0
External Forces	6	8.0×10^{-5}	9	1.2×10^{-4}
Weld	1	1.3×10^{-5}	2	2.7×10^{-5}
Surface Equipment	3	4.0×10^{-5}	1	1.3×10^{-5}
Joints	2	2.7×10^{-5}	0	0
Other	7	9.3×10^{-5}	2	2.7×10^{-5}
	24	3.2×10^{-4}	14	1.9×10^{-4}

Sources: ERCB (1991), Cassley (1991), Larson (1991).

[a] Frequency based on estimated total HVP pipeline length in service from 1975 - 1990 of 75,440 km·yr, which is an average of 4715 km of HVP pipeline in service per year.

Table 4. Representative meteorological conditions and their frequency of occurrence.

Code[a]	Stability	Wind Speed (m/s)	Frequency[b] (%)
C3	Unstable	3	17.6
D5	Neutral	5	49.1
E3	Stable	3	16.4
F1	Stable	1	16.9
			100.0

[a] Code identifies represenative meteorological condition for category, based on stability class and windspeed in m/s. For example, F1 identifies stability class F with windspeeds of 1 m/s (1 m/s = 3.6 km/h).

[b] See Table 2 for detailed breakdown.

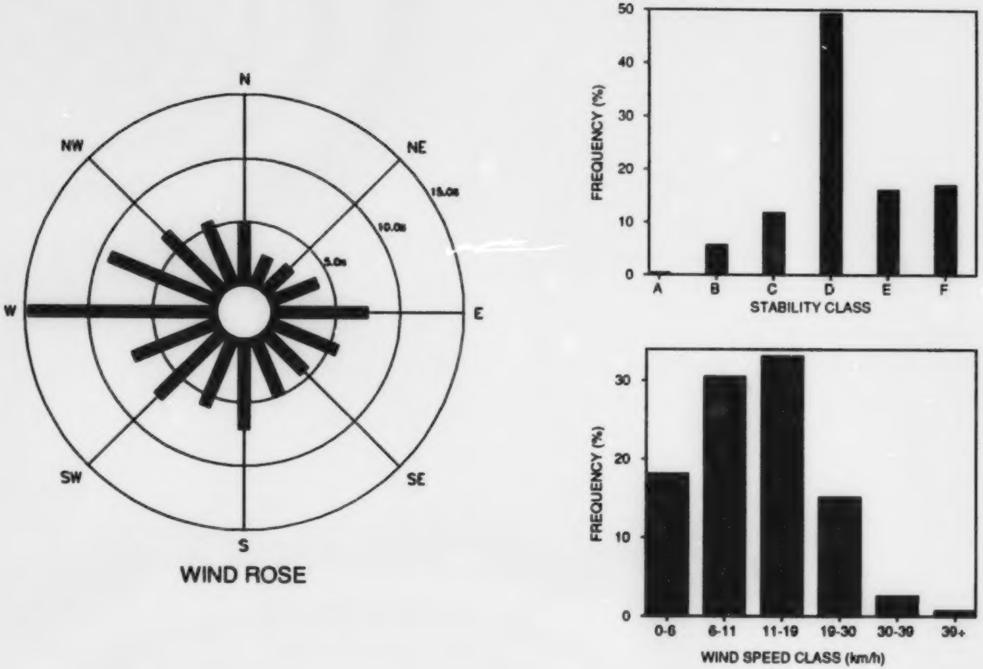

Figure 3. Frequencies of meteorological conditions for Namao, Alberta (1973 to 1984).

meteorological conditions selected to represent the range of annual weather conditions in the risk assessment.

2.3.3 Ignition Probabilities

The sequence of possible incidents following a release was shown schematically in the event tree given in Figure 2. The Health and Safety Executive (HSE) of the United Kingdom was the major source of information to quantify the probabilities of ignition (Crossthwaite *et al*, 1988). Each step in the event tree is discussed. Overall probabilities of hazardous incidents are given in Section 3.

Immediate Ignition

The probability of immediate ignition following a rupture is assumed to be 0.05. Immediate ignition leads to a fireball, followed by a jet fire. For a leak, the probability of immediate ignition is assumed to be zero.

Delayed Ignition

The probability of delayed ignition depends on the density of downwind ignition sources (e.g., residences) and the atmospheric stability. If a release were to occur in a rural area, the probability of ignition is much less than if it were to occur in an urban area. The probability of delayed ignition in stable weather is slightly less (0.9 times) than that of the probability of delayed ignition in neutral or unstable weather. This is to reconcile a larger flammable cloud area in stable weather with a wider but lower cloud and a likely lower density of ignition sources when stable weather occurs (generally at night). The assumed probabilities of delayed ignition for each condition are:

	Neutral Unstable	Stable
Urban	0.800	0.720
Rural	0.040	0.036

Explosive Conditions

The delayed ignition of a flammable cloud may, under certain circumstances, generate damaging overpressure blast waves as well as thermal radiation. A vapour cloud explosion results if overpressures are produced. Flash fires are more likely to make the transition to vapour cloud explosions if partial confinement and turbulence are present. The probabilities of explosive conditions vary with atmospheric turbulence and are:

	Neutral Unstable	Stable
Explosion	0.33	0.10
Flash Fire	0.67	0.90

SECTION 3

CONSEQUENCES AND FREQUENCIES

This section presents the estimated consequences and frequencies of hazardous incidents based on the methodology presented in Section 2. The frequency of each hazardous incident can be obtained by multiplying the release frequency by the incident probability. Results are presented for a full rupture (the worst possible release), a partial rupture (the worst credible release) and a leak (the most probable release). Probabilities are discussed for incidents in rural and urban areas. An evaluation of the risk to the public is presented in Section 4.

3.1 FULL RUPTURE

The frequency of full ruptures is 2.1×10^{-5} releases/km·yr, based on ERCB pipeline failure records.

3.1.1 Fireballs and Jet Fires

Consequences

Table 5 gives the distance from the release point to thermal radiation effect zones for a full rupture. If immediate ignition does occur, the initial fireball rapidly decays to a jet fire as NGL is released from the pipeline. The fireball has a mass of about 11 tonnes of NGL, would last approximately 10 seconds and have a diameter of about 130 metres. The fireball would be followed by a jet fire with a height of about 190 m. The jet fire would last approximately 15 minutes. As shown in Figure 4, the effect zones for jet fires are less than for the fireball.

Probabilities

The probability of immediate ignition leading to a fireball, if a rupture occurs, is 5%. The probability of a jet fire is the sum of the probabilities of a fireball, a flash fire and a vapour cloud explosion, as presented in Table 6. For a rural area the estimated probability of a jet fire, given a rupture occurs, is 9%. For a rupture in an urban area the probability of a jet fire is higher at 73% due to the higher number of potential ignition sources.

3.1.2 Flash Fires

Consequences

Figure 5 shows the effect zones for flash fires associated with a full rupture in a 15 km pipeline segment, under each of the four meteorological conditions considered. The black area is where the maximum concentration is above the UFL. The darker shaded area is where the predicted maximum NGL concentration is between the upper

Table 5. Thermal Radiation Effect Zones.

Effect[a]	Radiation Intensity (kW/m²)	Distance from Release (m) Fireball Full & Partial Rupture	 Jet Fire Full Rupture	 Partial Rupture	 Leak
Spontaneous ignition of wood after 45 s	25	130	50	20	6
Pain threshold reached after 8s, second degree burns after 20s	9.5	220	80	30	10
Safe - no discomfort after long exposures	1.6	520	200	70	20

na - not applicable to leaks.

[a] - World Bank (1985).

Table 6. Probabilities of Flash Fires, Vapour Cloud Explosions, Jet Fires, and No Ignition for Ruptures.

Meteorological Condition Code[a]	Rural Area Vapour Cloud Explosion	 Flash Fire	 No Ignition	Urban Area Vapour Cloud Explosion	 Flash Fire	 No Ignition
C3	0.0008	0.0016	0.0556	0.0153	0.0311	0.0116
D5	0.0047	0.0096	0.3447	0.0948	0.1925	0.0718
E3	0.0003	0.0023	0.0687	0.0051	0.0462	0.0200
F1	0.0003	0.0028	0.0843	0.0063	0.0566	0.0245
TOTAL	0.0095	0.0272	0.9133	0.1901	0.5446	0.2153

Probability of a Jet Fire is 0.0867 (0.0867 = 0.0500[b] + 0.0095 + 0.0272)

Probability of a Jet Fire is 0.7347 (0.7347 = 0.0500[b] + 0.1901 + 0.5446)

[a] See Table 4 for description of conditions

[b] The probability of a jet fire, following a fireball, under all meteorological conditions.

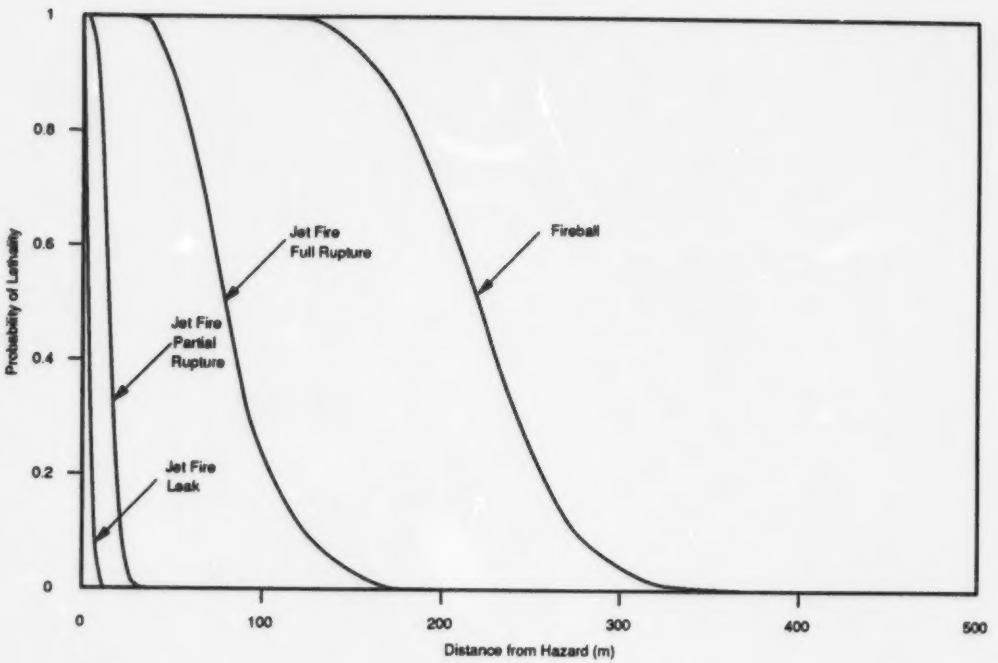

Figure 4. Probability of lethality from thermal effects in the vicinity of an NGL pipeline rupture.

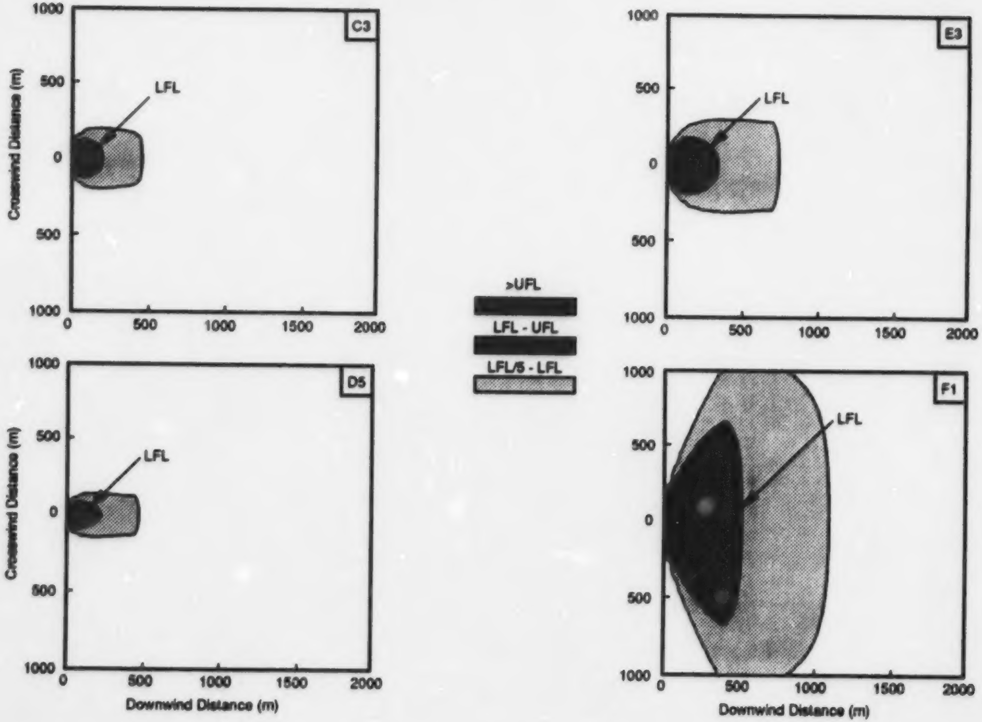

Figure 5. Predicted concentrations resulting from the full rupture of an NGL pipeline.

flammability limit (UFL) and the lower flammability limit (LFL). The outermost contour represents one fifth of the LFL.

It is conservatively assumed that people and buildings within the LFL contour would be exposed to direct flame contact and would not survive (TNO, 1988). The largest effect zones are associated with low wind speeds and stable atmospheric conditions. The maximum predicted downwind and crosswind distances to the LFL are 510 and 720 m, respectively and occur under F1 conditions.

For the higher wind speed conditions (C3, D5, E3) the predicted maximum downwind extent of the flammable area is reached while the release is occurring. At the lower wind speeds, the maximum cloud size occurs after the release has stopped. Effect zones would be smaller for releases from shorter segments under low wind speed conditions.

Probabilities

Table 6 gave the probabilities of flash fires, vapour cloud explosions, jet fires and no ignition, for each meteorological condition examined for rural and urban areas. The overall chance of a flash fire occurring due to a rupture in a rural area is about 3%. In an urban area, the chance of a flash fire if a rupture occurs is 54%, due to the higher density of potential ignition sources. The most likely flash fire is represented by meteorological condition D5.

3.1.3 Vapour Cloud Explosions

Consequences

In the event of a vapour cloud explosion, it is assumed that no one survives if they are within the LFL contour (TNO, 1988) shown in Figure 5. The pressure wave created by the explosion can also cause damage to people and buildings. Table 7 summarizes the distances to selected overpressure effects from the predicted epicentres of the explosion for a full rupture. Also included in the table is the size of the cloud, the downwind distance to the epicentre and the explosive mass of the cloud.

The least favourable meteorological condition is low wind speed stable class F1, as this results in the largest explosive mass of 124 t. The total mass of NGL released from a 15 km section is 366 t. The most favourable meteorological condition D5 results in the minimum explosive mass of 9 t. The effect zones increase with the explosive mass of the cloud, as can be seen in Figure 6.

The distance to a 50% chance of eardrum damage corresponds to nearly complete destruction of houses. People outdoors may experience eardrum damage; however, if they were indoors they would be wounded or become fatalities due to the building collapsing on them. People within the 10 kPa peak overpressure effect zone may be wounded (TNO, 1988).

Table 7. Cloud Size and Overpressure Effect Zones for Full Rupture.

		Meteorological Condition Code[a]			
		C3	D5	E3	F1
Cloud size to LFL					
Length	(m)	200	220	320	510
Half-width	(m)	140	90	200	720
Area	(ha)	4.1	2.6	9.2	49.7
Downwind Distance to Epicentre	(m)	90	90	130	240
Explosive Mass	(t)	14	9	27	124

Effect[b]	Peak Overpressure (kPa)	Distance from Epicentre (m)			
Fatalities, total destruction of buildings	100	within LFL contour shown in Figure 5			
Wounded with a 50% chance of eardrum damage, nearly complete destruction of buildings	43	140	120	170	270
Wounded by mechanical damage, repairable building damage	10	380	310	470	780
Safe distance,10% chance of glass breakage, no serious building damage	2	1190	1020	1460	2460

[a] See Table 4 for description of conditions.

[b] Clancey (1972).

Probabilities

The probabilities of vapour cloud explosions were presented in Table 6. If a rupture were to occur in a rural area, there is less than a 1% chance of an explosion. However, if the release were to occur in an urban area, the probability of a vapour cloud explosion increases to 19%. The most likely scenario is represented by meteorological condition D5.

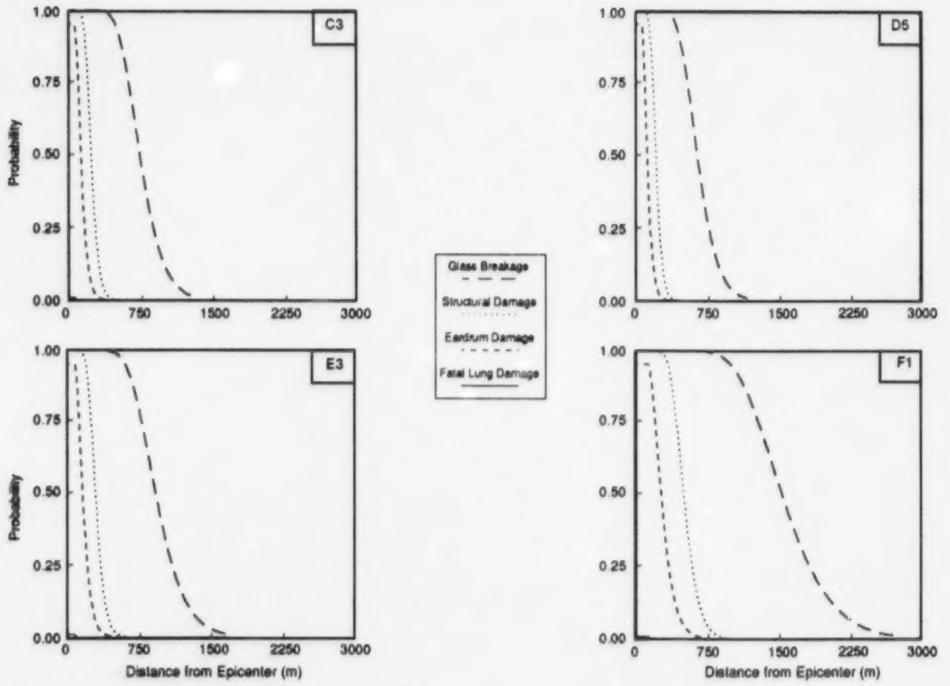

Figure 6. Overpressure effects resulting from the explosion of the predicted maximum flammable mass of NGL vapour dispersed from a full rupture.

3.1.4 No Ignition

Consequences

The black area shown in Figure 5 is where the NGL concentration exceeds the UFL and conservatively represents the asphyxiation effect zone. The effect zones occur near the source. A person near the source would most likely flee the area to safety upon recognizing that a rupture has occurred. If the cloud is not ignited and there is no one near the source, the cloud safely disperses into the atmosphere.

Probabilities

For asphyxiation to occur, a person must be within the black shaded area and the release must not be ignited. The probabilities of non-ignition for an NGL pipeline rupture were given in Table 6. There is a 91% chance that an NGL cloud is not ignited in rural areas along pipelines. If the pipeline were located in an urban area, the chance that the cloud is not ignited is 22%.

3.2 PARTIAL RUPTURE

The frequency of partial ruptures is 1.7 x 10^{-4} releases/ km·yr, based on ERCB pipeline failure records.

3.2.1 Fireballs and Jet Fires

Consequences

The distance to thermal radiation effect zones for the partial rupture were given in Table 5 and Figure 4. The fireball for a partial rupture is the same as for a full rupture. The jet fire for a partial rupture would have a height of about 60 m and would last approxmately two and one-half hours.

Probabilities

The probabilities of a flash fire following a partial rupture are the same as for a full rupture, as given in Table 6.

3.2.2 Flash Fires

Consequences

Figure 7 shows the effect zones associated with a partial rupture under the four meteorological conditions considered. The contours for the partial rupture look similar to the contours for a full rupture given in Figure 5, except the downwind and crosswind extent of the cloud is considerably less for the partial rupture. People and buildings within the LFL contour would be exposed to direct flame contact and may not survive. The largest effect zones are associated with low wind speeds and stable

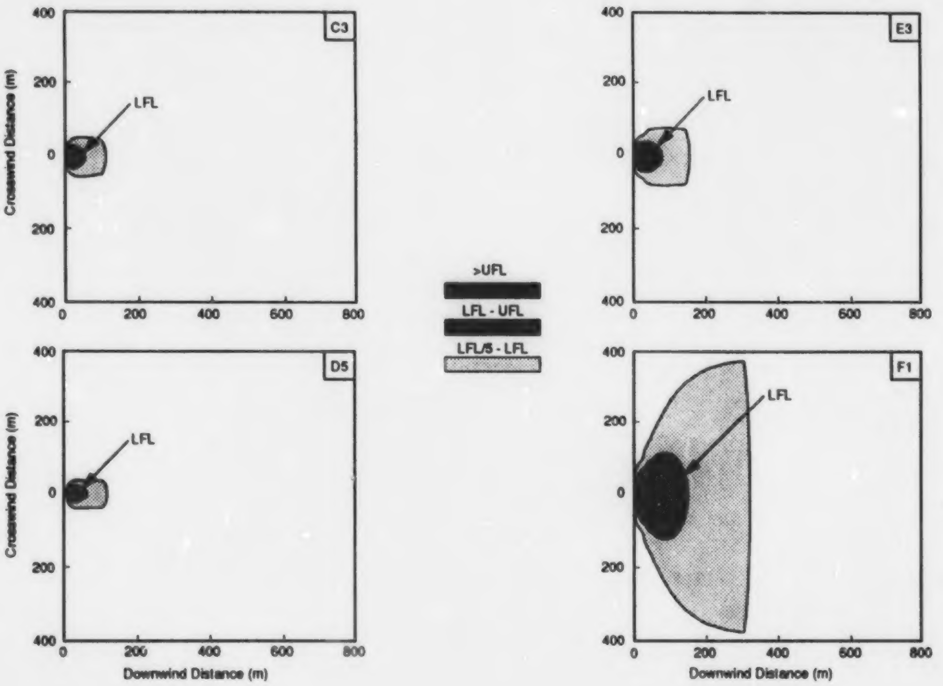

Figure 7. Predicted concentrations resulting from the partial rupture of an NGL pipeline (note scale change from Figure 5).

atmospheric conditions. The maximum predicted downwind and crosswind distances to the LFL are for meteorological condition F1 and are 150 and 130 m, respectively.

The maximum downwind extent of the flammable cloud under all meteorological conditions is predicted to occur while the release is still occurring. Effect zones for a partial rupture do not change with the pipeline segment length.

Probabilities

The probabilities of flash fires following a partial rupture are the same as for a full rupture, as given in Table 6.

3.2.3 Vapour Cloud Explosions

Consequences

In the event of a vapour cloud explosion during a partial rupture, it is assumed no one survives if they are within the LFL contour as shown in Figure 7. Table 8 and Figure 8 summarizes the distances to selected overpressure effects.

The least favourable meteorological condition is low wind speed stable class F1 which results in the largest explosive mass of 3.5 t. The total mass of the NGL released from the longest section is 366 t, the same as for a full rupture. The maximum cloud size forms early in the release and does not increase with time. At the lower flow rates associated with a partial rupture, the NGL is rapidly dispersed into the atmosphere resulting in a smaller flammable cloud size.

The most favourable meteorological condition D5 results in the minimum explosive mass of 0.3 t. Note that for the high wind speed conditions (C3, D5, E3) the explosive mass is less than the ignition threshold mass of 1 t and ignition may not lead to an explosion (AIChE, 1989).

Probabilities

The probabilities of vapour cloud explosions following a partial rupture are the same as for a full rupture, as given in Table 6.

3.2.4 No Ignition

Consequences

The black area in Figure 7 represents where the NGL concentration exceeds the UFL and where people may be asphyxiated. The effect zones are near the source. A person near the source would most likely flee the area to safety upon recognizing that a rupture has occurred. If the cloud is not ignited and there is no one near the source, the cloud safely disperses into the atmosphere.

Table 8. Cloud Size and Overpressure Effect Zones for Partial Rupture.

		Meteorological Condition Code[a] C3	D5	E3	F1
Cloud size to LFL					
Length	(m)	50	60	80	150
Half-width	(m)	30	20	40	130
Area	(ha)	0.3	0.2	0.5	2.6
Downwind Distance to Epicentre	(m)	30	30	30	60
Explosive Mass	(t)	0.4[b]	0.3[b]	0.7[b]	3.5

Effect[b]	Peak Overpressure (kPa)	Distance from Epicentre (m)			
Fatalities, total destruction of buildings	100	within LFL contour shown in Figure 7			
Wounded with a 50% chance of eardrum damage, nearly complete destruction of buildings	43	50	40	40	90
Wounded by mechanical damage, repairable building damage	10	120	110	140	240
Safe distance,10% chance of glass breakage, no serious building damage	2	350	330	440	750

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[a] See Table 4 for description of conditions.

[b] Note predicted explosive mass is less than the ignition threshold mass of 1 t and ignition may not result in explosion.

[c] Clancey (1972).

Probabilities

The probability of no ignition for a partial rupture release are the same as for a full rupture, as given in Table 6.

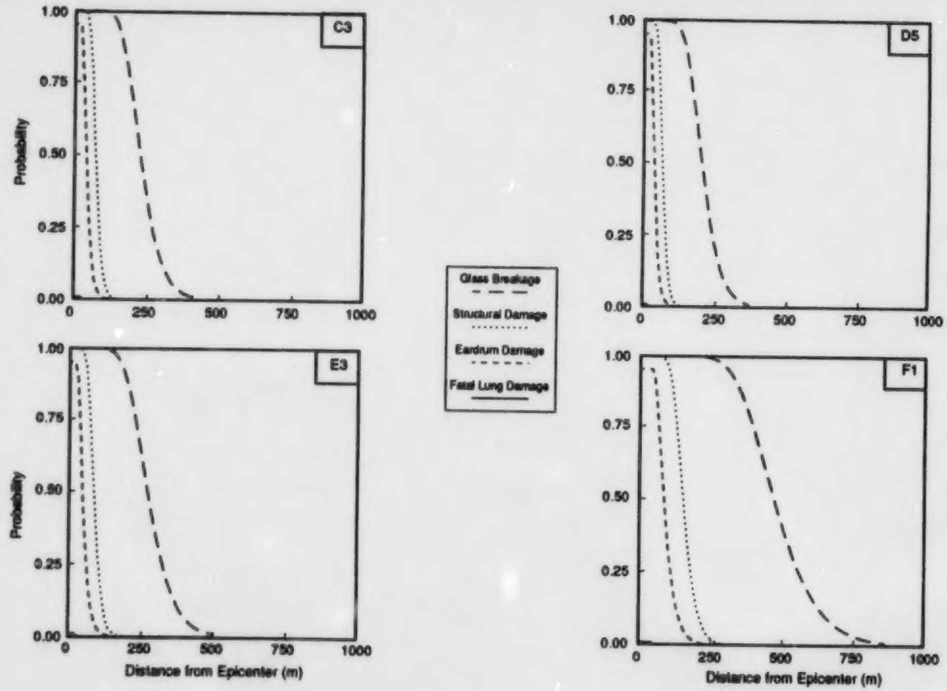

Figure 8. Overpressure effects resulting from the explosion of the predicted maximum flammable mass of NGL vapour dispersed from a partial rupture (note scale change from Figure 6).

3.3 LEAK

The most probable release is a leak from the pipeline. The frequency of leaks is 3.2 x 10^{-4} releases/km·yr, based on ERCB pipeline failure records. This is about double the partial rupture frequency.

Referring back to the event tree given in Figure 2, a fireball cannot result from a leak because the release rates are too low and immediate ignition is not assumed to occur. Vapour clouds formed as a result of a leak are less than the ignition mass threshold of 1 t, and ignition will not lead to an explosion.

3.3.1 Jet Fires

Consequences

The distance of thermal radiation effect zones for a leak were given in Table 5 and Figure 4. The jet fire for a leak would have a height of about 18 m. The jet fire could last about one day unless other actions are taken to reduce the loss of product.

Probabilities

The probability of a jet fire is the same as that for a flash fire, as given in Table 9. In a rural area about 4% of leaks are expected to be ignited and result in a jet fire. This compares to 77% in an urban area.

3.3.2 Flash Fires

Consequences

Figure 9 gives the spatial extent of the vapour cloud resulting from a leak, under the four meteorological conditions considered. As for ruptures, the least favourable meteorological conditions are low wind speed, stable atmospheres (F1). Persons and/or equipment within the flammable range which may ignite the cloud would most likely not survive the flash fire.

Probabilities

The probabilities of flash fires are given in Table 9 and are the same as those for a jet fire.

3.3.3 No Ignition

Consequences

Asphyxiation from a leak is not considered possible due to the very small localized area which would exceed the UFL.

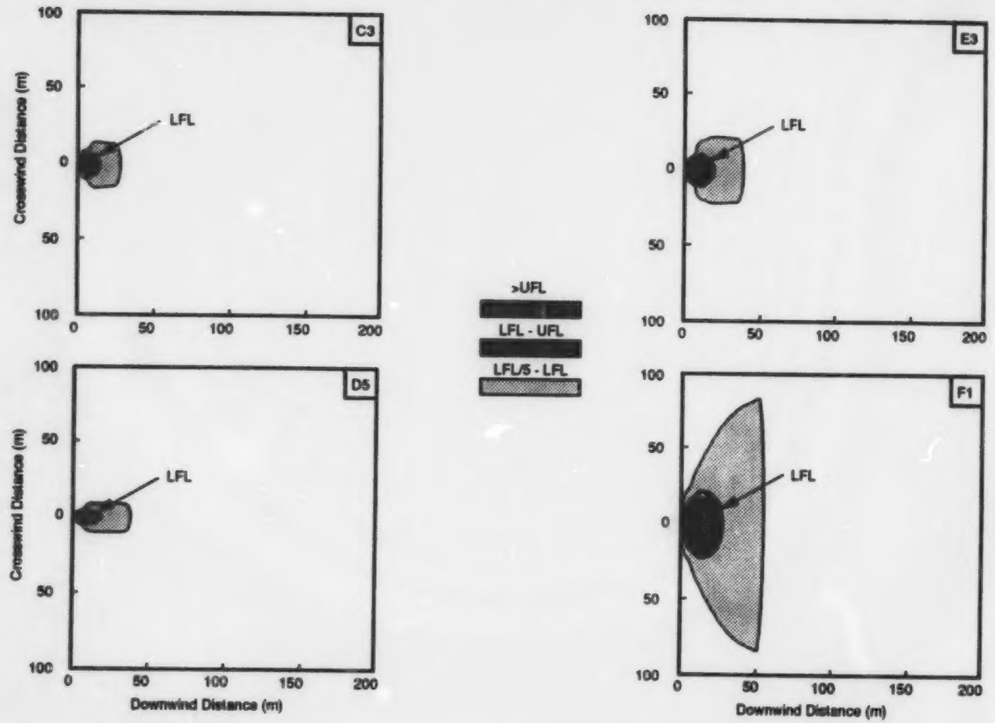

Figure 9. Predicted concentrations resulting from a leak in an NGL pipeline (note scale change from Figure 5).

Probabilities

The probability of a leak not being ignited is 96% in a rural area and 23% in an urban area.

Table 9. Probabilities of Flash Fires, Jet Fires and No Ignition for Leaks.

Meteorological Condition Code[a]	Rurual Area		Urban Area	
	Flash Fire Jet Fire	No Ignition	Flash Fire Jet Fire	No Ignition
C3	0.0070	0.1690	0.1408	0.0352
D5	0.0196	0.4714	0.3828	0.0982
E3	0.0059	0.1581	0.1181	0.0459
F1	0.0061	0.1629	0.1217	0.0473
TOTAL	0.0387	0.9613	0.7734	0.2266

NOTE: The probability of a fireball and vapour cloud explosion for a leak are assumed to be zero.

[a] See Table 4 for a description of conditions.

SECTION 4

RISK ESTIMATION AND ASSESSMENT

Up to this point, risk has been treated as independent triplet combinations of hazardous incident, frequency and consequences. Risk analysis is the process of combining the estimated consequences and likelihood of the selected hazardous incidents to provide a quantitative measure of risk. Risk assessment is the process by which these results are used to make decisions. To provide some perspective on the estimated levels of risk, and to assist parties interested in evaluating the acceptability of these risks, information on common risks and risk criteria is provided.

4.1 RISK CRITERIA

Decisions with respect to the acceptability of risk are personal and social value-judgements, involving the public exposed to the risks, government agencies and the industrial proponent of the risk-producing project. Guidelines relating to criteria on the acceptability of public risk from hazardous facilities do not exist in Alberta.

Canada's Major Industrial Accident Coordinating Committee working group on land use planning and control have recently published their proposed risk criteria (MIACC, 1991). Their individual risk criteria for land use planning are summarized in Table 10 and are based on consideration of criterias adopted in the U.K. and the Netherlands. These criteria assume an effective emergency response plan is in place. If not, the individual risk level shown in Table 10 should be decreased by a factor of 10 (i.e. 100 chances in a million becomes 10 chances in a million).

Toronto City Council recently adopted that the upper bound of acceptable risk along rail corridors is 10 chances in a million (City of Toronto, Planning and Development Department, 1991).

Table 10. MIACC's Proposed Risk Criteria for Land Use Planning.

Individual Risk Levels (chances in a million of a fatality per year)	Adjacent Land Use[a]
Above 100	No other land uses than the source facility.
Between 100 to 10	Uses involving continuous access and the presence of limited numbers of people but easy evacuation, e.g., parks, warehouses, manufacturing plants.
Between 10 to 1	Uses involving continuous access but easy evacuation, e.g., commercial uses, low-density residential areas, offices.
Below 1	All other land uses without restriction including institutional uses, high-density residential areas, etc.

[a] These risk criteria assume that an effective emergency response plan is in place. Otherwise, decrease the risk levels by a factor of 10.

Source: MIACC (1991).

4.2 RISK ESTIMATION

Risk estimation is a method of risk analysis in which assumptions are made to simplify the complex calculation procedure. The assumptions result in conservative (i.e., higher) risk estimates. Pipeline risk analysis is especially difficult because a receptor can be effected by releases anywhere along the pipeline within the distance of the effect zone.

Individual risk is defined as the annual chance of fatality a receptor is exposed to from all hazardous incidents. Flash fires and vapour cloud explosions are the major hazards which have the potential to cause fatalities or totally destroy buildings. The probability of lethality from fireballs and jet fires is also significant near the pipeline. Injuries are not used as a criterion because of the difficulty in determining the degree of severity. Fatalities have been traditionally used for risk assessments of accidental releases. The probability of totally destroying buildings is equivalent to the probability of fatality.

An important parameter in determining the risk to a receptor is the "interaction length". This is the length of pipeline, that, if a release were to occur within, would expose a receptor to the hazard. The interaction length (m) for a hazard decreases with distance from the pipeline. It is multiplied by the release frequency (releases/m · yr), the incident probability (incidents/releases) and the probability of lethality (fatalities/ incident) to obtain the individual risk (probability of fatality/year).

The incident probability of fireballs and jet fires are assumed to be independent of the weather and wind direction. However, for flash fires and vapour cloud explosions, the incident probability also accounts for the wind direction and meteorological condition probability.

A receptor does not have to be directly downwind of the release, on the plume centerline, to be effected. Both the downwind and crosswind extents of the plume must be considered. A box shaped plume was used in the analysis, thus overestimating the effected area. Winds from all directions can result in receptors being effected. A uniform, 16 point wind rose was assumed.

The consequences and frequencies associated with the three release scenarios and the four meteorological conditions were used. Risks in rural and urban areas were estimated, assuming the receptor is at the location for 100% of the time.

Estimates of individual risk were made for various distances from the pipeline, as shown in Figure 10. Individual risk is a maximum on the pipeline and decreases with distance from the pipeline. Within the pipeline right-of-way, the maximum risk is 5 and 30 chances in a million of fatality per year for rural and urban areas, respectively.

The risk of fatality in a rural area 200 m from the pipeline is about 2 chances in a million per year. For an urban area about 200 m from the pipeline, the risk of fatality is about 4 chance in a million per year. At about 300 m from the pipeline in a rural area, the risk of fatality is less than 0.1 chances in a million and is considered to be negligible. In an urban area, the risk is negligible about 800 m from the pipeline.

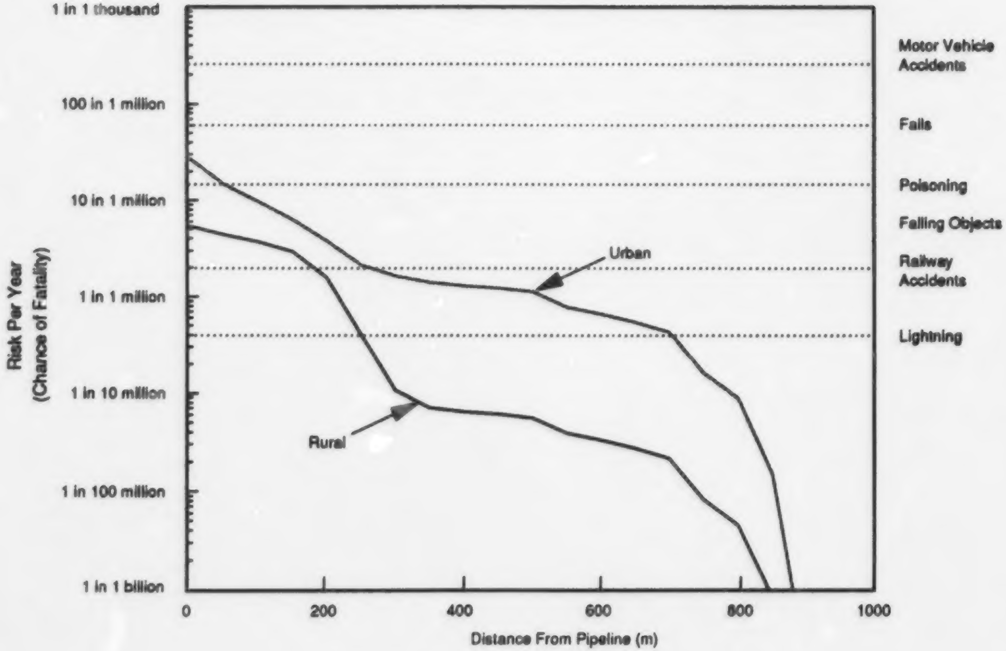

Figure 10. Individual risk to permanent residents in rural and urban areas due to an NGL pipeline.

4.3 RISK ASSESSMENT

One way to understand the magnitude of a risk is to compare it with other risks. Therefore, also shown on Figure 10, for comparative purposes, are the individual risk levels for common risks in Alberta. These data are based on fatality statistics compiled by Statistics Canada for the 10 year period 1978 to 1987.

Referring to the proposed MIACC risk criterias for land use planning (Table 10), individual risk levels between 100 and 10 chances in a million would be applicable to areas where there is continuous access and the presence of a limited number of people with easy evacuation. Risk levels less than 10 chances in a million would be applicable to areas with low to high population densities. These criteria of acceptability are based on having an effective emergency response plan.

The individual risks for rural areas are less than 10 chances in a million. For an urban area, the individual risk is less than 10 chances in a million at a distance of about 100 m from the pipeline. At closer distances to the pipeline the risk increases but does not exceed 100 chances in a million. Risks associated with NGL pipelines can be made acceptable, based on MIACC's proposed risk criteria, by adopting appropriate land use guidelines. Setback distances and emergency response plans will reduce the risk to the public.

4.4 CONCLUDING REMARKS

In summary, the estimated levels of individual risks from a typical NGL pipeline are comparable or less than involuntary risks faced by Albertans in everyday life. Risks in rural areas meet the criteria proposed by MIACC. In urban areas, land use planning criterias proposed by MIACC must be adopted in order to reduce the risk to the public.

The risk estimates of this study have been made on the basis of cautious estimates, and conservative assumptions have been made throughout the analysis. In particular, the historical failure frequency was used and a lower chance of release is expected. Therefore, the actual risks would be expected to be lower than those presented.

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IGLOU 1.0 :
a Canadian Decision Support System Designed For Chemical Spills Prevention, Preparedness and Response.

by

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The IGLOU Decision Support System has been developed within the PIGES project. The PIGES project is the brainchild of the Quebec City Region Community Health Network. This project was set up after the evaluation of the world's largest open air PCB fire that took place in St-Basile-le-Grand, Québec, Canada in August 1988[1].

The evaluation of this disaster has shown that the cost (more than 40 million Can$) would have been much lower if the first responders had been in a position to gain access rapidly to the thematic and cartographic information required to manage such a fire[2].

The PIGES project has been funded at the federal level by Emergency Preparedness Canada (EPC-PCC) and in Quebec by the Ministries of the Environment (MENVIQ), Health and Social Services (MSSS) and Public Safety (MSPQ).

The main goal of this project is :
- to facilitate, through better information management, the development and updating of local and regional emergency measures plans, particularly in the technological

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[1] Denis, H., La gestion de catastrophe : Le cas d'un incendie dans un entrepôt de BPC à St-Basile-le-Grand, Département de génie industriel, École Polytechnique, Université de Montréal, Montréal, Québec, 1989.

[2] Godon, D., Guerrier, P., Leroux, R., The PIGES project, Fourth International Symposium in Medical Geography, Norwich, England, July 16th-19th, 1990, 39 p. (Paper available at DSC-CHUL).

accidents category;
- to improve, through better integration of thematic and mapping data, the efficiency of emergency responses to protect public health and the environment;
- to reduce, through better access to information about hazardous materials, mortality and morbidity among responders and the general public, as well as the cost of a technological accident[3].

The PIGES project is co-ordinated by the Community Health Department of Laval University Hospital Centre (DSC-CHUL). So far, at the regional and local levels, this project has also been financed by le Centre de Toxicologie du Québec (CTQ), the Quebec City Region Health and Social Services Council (CSSS-03), the St-Sacrement Hospital Community Health Department (DSC-HSS), by the City of Quebec, the Port of Quebec Corporation, as well as by the private firms DAISHOWA Inc. and INTERTANK-IMTT Inc. The PIGES project is supported as well by the Environmental Health Committee of the Quebec Community Health Deparments (CSE). The total budget (1989-1992) was 400 000 CAN$.

The first version of IGLOU, IGLOU 1.0, has been conceived to act as a Decision Support System (DSS) among the partners participating in the PIGES project. IGLOU 1.0 is an application built with a Relational Database Independent Development Environment, OMNIS® 5 (recently upgraded to OMNIS® Seven 1.0) and integrated to a Geographic Information System (GIS) software, MapInfo® 1.1.3 [4].

OMNIS®, distributed by Blyth Software (a British company), is the world's only Database Independent Development Environment that runs interoperably on both

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[3] Emergency Preparedness Digest, The PIGES project, p.22, Vol. 19, N°1, January-March 1992.

[4] Godon, D., Guerrier, P., Auger, D., Mercier, S., IGLOU : A Canadian Tool based on Relational Database Management and GIS technology and designed for Emergency Planning, Emergency Planning' 91 Conference, Lancaster University, Lancaster, England, 8th-10th, Papers and Abstracts, 92 p., 1991.

Apple Macintoshes™ and Windows™ based IBM-PCs and compatibles : Databases developed on either platform can be seamlessly converted to the other and the same database can be shared on a network containing both Apple Macs and Windows machines. OMNIS® was chosen for the development and the support of IGLOU 1.0 because it provides a powerful and easy-to-use application that can be implemented in workgroups or organizations with distributed data topologies. IGLOU 1.0 has been designed for local and LAN-based management. Based on OMNIS® 7, it has the potential to allow cooperative processing requiring SQL access (SQL is the industry standard for mini-computer and mainframe databases).

MapInfo®, distributed by MapInfo Corporation (an American company), is a desktop mapping software which allows users to overlay databases onto maps and perform powerful "What if ?" geographic analyses of these data to reach decisions faster and easier. Integrated to IGLOU 1.0 relational database, MapInfo® improves the way IGLOU users manage information: they can analyze their data graphically (such as searching for resources within a given radius or within a boundary) and spot trends and opportunities for Chemical spills prevention, preparedness and response stages they may have otherwise missed. MapInfo® has multi-platform compatibility and allows to use SQL.

Based on these two multi-platform software products, IGLOU 1.0 runs in two current computer environments :
- Apple™ Macintosh with Operating Systems 6 and now 7;
- IBM™ and compatibles with Windows 3.0 and now 3.1 Operating Systems.

IGLOU 1.0 has been based mainly on the U.S. Environmental Protection Agency's expertise in the field of Chemical Emergency Preparedness and Prevention. IGLOU 1.0 integrates the Response Information Data Sheet (RIDS) and

Codebreaker chemical databases which are already used in the well-known American program CAMEO™ 3.0 (Computer-Aided Management of Emergency Operations) [5]. In a near future, IGLOU will allow the use of ALOHA™, the plume dispersion modeling program developed by NOAA and the U.S. EPA. Already available on the Mac, this program should run on Windows this year.

The French version of IGLOU 1.0 is currently used by the DSC-CHUL to manage the geocoded computerized inventory set up within the PIGES pilot-project developed in Quebec City. This inventory gathers together the information required for the prevention, preparedness and response stages of potential chemical spills and other types of technological accidents which may occur in Quebec City. Quebec City was chosen by the PIGES project team to carry out the pilot project which is based on the United Nations Environment Programme (UNEP) APELL Process recommendations [6]. Implementation of IGLOU 1.0 among the PIGES project financial partners should start during the present year.

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[5] Blotzer, M.J., IH Interface. CAMEO™ 3.0 for Macintosh. ALOHA. Appl. Occup. Environ. Hyg. 6(8), pp. 648-649, August 1991.

[6] UNEP, Industry and Environment Office, APELL : Awareness and Preparedness for Emergencies at Local Level - A Process for Responding to Technological Accidents. UN Publication Sales, N° E.88.III.D.3, 1988.

SPILL REPORTING: NEW DEVELOPMENTS IN THE LAW

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I. INTRODUCTION

Provincial, municipal and federal statutes may impose legal obligations on manufacturers, handlers, users and transporters of waste or of toxic or regulated chemicals. These obligations often include duties to report spills and discharges, prevent further damage, clean-up spills, restore the environment and pay compensation to those who have suffered damage as a result of a spill.

Directors, officers and employees may be charged with environmental offences whether or not that company is prosecuted. Companies and individuals may also be ordered to undertake clean-up and prevention programs, and to pay the costs of government action.

Statutory obligations and consequent costs can apply to everyone in the chain of ownership, management or control of a spilled chemical, even if the company or individual was not at fault, or involved with the spill. This paper begins with a description of the federal, provincial and municipal statutory framework governing the prohibition of spills and the reporting obligations when spills occur. We have used Ontario as the example of provincial and municipal regulation, and the Canadian Environmental Protection Act as the example of federal regulation.

The latter part of the paper highlights new developments in the law affecting spill reporting and the significance the cases have to the manner in which spills are reported.

II. STATUTORY FRAMEWORK

A. ONTARIO LEGISLATION[1]

The following provincial statutes are among those that create significant legal obligations in Ontario:

1. Environmental Protection Act (EPA), R.S.O. 1990, c.E-19
   -Regulation 308 (EPA)-Air Pollution, R.R.O. 1980, Reg. 308
2. Ontario Water Resources Act (OWRA), R.S.O. 1990, c.O-40
3. Pesticides Act, R.S.O. 1990, c.P-11
4. Dangerous Goods Transportation Act, 1981, R.S.O. 1990, c.D-1
5. Occupational Health and Safety Act, R.S.O. 1990, c.O-1
   -Workplace Hazardous Materials Information System (WHMIS) Regulations, O.Reg. 643/88,O.Reg 644/88

The EPA regulates discharges of contaminants and spills of pollutants into the environment. EPA Regulation 308 governing air emissions contains specific reporting requirements for emissions resulting from process start-ups, shut-downs and upsets.

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[1] References in the text to Ontario Statutes are to the Revised Statutes of Ontario, 1990.

The Act imposes duties on those who own or control regulated contaminants or contaminants which may cause adverse effects. The Act also stipulates that current or former owners of the land or business can be responsible for pollution prevention and clean-up.

The EPA applies to most discharges and spills which are subject to the OWRA: this paper concentrates on the provisions of the EPA.

B. MUNICIPAL REGULATORY POWERS

Most municipalities of significant size have sewer-use by-laws which regulate or prohibit the discharge of excess quantities of storm water or contaminants into municipal drainage works or sewers. Each municipality may have its own by-laws and standards, although many have enacted sewer-use by-laws based on the provincial model.

Sewer-use by-laws create offences which can be punishable by substantial fines.

These by-laws usually require notification of municipal authorities, often through the municipal public works (or environmental) departments. It is not uncommon to find that public works or municipal environmental officials are the first to detect, respond to or investigate a spill.

Investigations related to alleged sewer use by-law infractions sometimes lead to involvement of MOE officials and result in charges under provincial statutes with even greater potential penalties.

C. FEDERAL LEGISLATION

The following federal statutes are some of those that regulate environmental matters:

1. Canadian Environmental Protection Act (CEPA), R.S.C. 1985, c.16
2. Fisheries Act, R.S.C. 1985, C. F-14
3. Transportation of Dangerous Goods Act, R.S.C. 1985, C.T-19
4. Pest Control Products Act, R.S.C. 1985, C.P-9
5. Canada Shipping Act, R.S.C. 1970, C.S-9

Environmental protection legislation is primarily monitored and enforced by municipal and provincial officials. The most significant federal environmental protection legislation for businesses (other than carriers) is the Canadian Environmental Protection Act. In this paper the reporting obligations under CEPA only are dealt with.

III. ENVIRONMENTAL EVENTS: WHEN IS A REPORT REQUIRED?

A. TOXIC SUBSTANCES, CONTAMINANTS AND POLLUTANTS

1. EPA - Contaminants and Pollutants

The EPA asserts jurisdiction over "discharges" of "contaminants" and "spills" of "pollutants". The definition of "contaminant" is comprehensive; it includes solids, liquids, gases, noise, heat and radiation that may cause an adverse effect. Any discharge of a contaminant which exceeds regulated standards must be reported (s.13(1)). If any discharge of a contaminant causes or is likely to cause an adverse effect, the Ministry must be notified (s.15(1)).

Part X of the EPA (formerly Part IX), known as the Spills Bill, establishes more onerous duties where a "spill" of a "pollutant" occurs. A pollutant is defined as a contaminant (a substance likely to cause an adverse effect) not including heat, sound or radiation. A spill is a separately defined event, and is discussed below.

2. Municipal Sewer Use By-Laws

Section 210(150) of the Municipal Act authorizes municipalities to pass sewer use by-laws.

> s.150. For prohibiting, regulating and inspecting the discharge of any gaseous, liquid or solid matter into land drainage works, private branch drains and connections to any sewer, sewer system or sewage works for the carrying away of domestic sewage or industrial wastes or both, whether connected to a treatment works or not.

Sewer-use by-laws enacted under this authority generally follow the provincial model sewer-use by-law which requires notification in the following circumstances:

> 1. a discharge or deposit of sewage not in the ordinary course of events, or of substances prescribed in the by-law, into any land drainage works, private branch drains or connections to combined or sanitary sewers;

2. a discharge or deposit of uncontaminated water or storm water, or of substances prescribed in the by-law, into any land drainage works, private drains or connections to any storm sewer.

Prescribed materials listed in the by-law generally include fuels, pesticides, toxic or radioactive materials, and hazardous, pathological and PCB wastes.

Sewage means any liquid waste containing animal, vegetable, mineral or chemical matter in solution or in suspension, except uncontaminated water.

While the wording of the by-law may absolutely prohibit some types of discharge and require a report in respect of a discharge of any quantity, municipal officials sometimes interpret the by-law according to provincial guidelines. For example, process cooling water incidentally contaminated with small amounts of hazardous chemicals could be interpreted as hazardous waste on strict reading of the by-law. However, municipal officials may refer to the Ministry of the Environment Guidance Manual for Generators of Liquid Industrial and Hazardous Work (January, 1991) together with Regulation 309. It is arguable that water incidentally contaminated with trace amounts of hazardous chemicals need not be automatically designated as hazardous waste.

3. CEPA - Toxic Substances

Regulations under CEPA establish minimum amounts of specific classes of chemicals which must be regarded as spills. A discharge in excess of the minimum will trigger reporting and clean up obligations.

CEPA regulations prescribe several classes of chemicals over which the federal government asserts jurisdiction to order reporting, clean-up and restoration and to impose sanctions. Currently regulations are in place designating certain substances "toxic". A substance is "toxic" if it enters the environment in quantity, concentration, or under conditions which may have an immediate or long term harmful effect on the environment or constitute a danger to human life, health or the environment on which human life depends.

The federal Minister of the Environment is permitted to make an interim order designating a substance toxic if the Minister believes it is toxic or not adequately regulated and that immediate action is required to deal with a significant danger to the environment or human life or health.

B. DISCHARGE, RELEASE, SPILL OR EMISSION

1. EPA - Discharge, Spill and Emission

a) Discharge

Section 14(1) of the EPA prohibits any person from discharging or causing or permitting a discharge of a contaminant into the natural environment that causes or is likely to cause an adverse effect.

A discharge includes a addition, emission, deposit or leak that enters the natural environment. A leak inside a building that does not give off fumes into the air and is cleaned up and disposed of before entering the sewer or soil has not entered the natural environment. The EPA does, however, make an exception for discharges into containment buildings (secondary discharges). (EPA s.2)

Whenever a contaminant is discharged that exceeds regulated amounts or concentrations or is likely to cause an adverse effect notification must be made to the MOE.(EPA ss. 13(1) and 15(1))

b) Spill

The spills provisions in Part X of the EPA impose more onerous requirements for the owners and controllers of pollutants which are spilled than those imposed under sections 13(1) and 15(1) respecting discharges of contaminants.

Section 91(1) defines a "spill" as a discharge of a pollutant:

i) that enters the natural environment,

ii) from or out of a structure vehicle or other container, and

iii) that is abnormal in quality or quantity in light of all of the circumstances of the discharge.

If a spill causes or is likely to cause an adverse effect on the natural environment or on the health, safety, comfort or business of people, the owner, controller and anyone who causes or permits the spill must comply with all of the requirements of Part X.

Subject to provisions in O.Reg. 618/85 a spill need not be reported if:

1. it does not escape from the building in which it was spilled (EPA s.2);

2. the amount is so small that it is not likely to cause any environmental damage (EPA s.92(1);

3. the spill is planned, the Director is notified, and preventative measures are taken so that no adverse effects can occur(O.Reg. 685/85 Part V); or

4. it is from the operating system of a vehicle(O.Reg. 685/85 Part V[2]).

The EPA does not establish, by regulation or otherwise the quantity of pollutant that must escape into the natural environment in order to trigger the obligation to report. In contrast, the Spill Reporting Regulation under British Columbia's Waste Management Act contains a schedule which classifies chemicals and sets out minimum quantities for spills which must be reported. If a quantity in excess of the scheduled amount is spilled, a report must be made.

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[2] s. 20. The spill must be under 100 litres, does not and is not likely to enter groundwater. The person having control must comply with the notification requirements under the Highway Traffic Act.

The Ontario Ministry considers that a spill into sanitary sewers may be considered to have entered the natural environment if the chemical spilled will volatilize within a sewage treatment plant, or if its potential for adverse environmental effects are not likely to be neutralized by treatment before discharge into receiving waters.

Notification of a spill or discharge may be followed by a Ministry investigation and the subsequent laying of charges. It is, therefore, necessary for environmental managers to try to determine in advance whether adverse effects may result from spills of various sizes and substances in the context of their operations. It is worthwhile to consult local Ministry of the Environment officials for assistance in establishing a spills reporting policy.

It is also important to understand that the local abatement officers and the investigators from Investigation and Enforcement Branch (IEB) are independent of each other. An opinion or undertaking given by an abatement officer as to what size of spill need not be reported will not bind an IEB investigator who may support a prosecution.

Since reporting statistics are kept by provincial spill reporting centres, the conservative 'report everything' approach may backfire. A company that attempts to be conservative or safe by reporting every event, no matter how small, will soon have a significant 'batting average' and may attract undue attention from enforcement officials.

Designation and training of staff as part of a spill response program is the best way to limit liability. Properly trained personnel should be able to determine whether a spill must be reported. In the event the company is prosecuted for failure to report, evidence that the spill response plan was carefully thought out, reasonable and was complied with by all designated personnel may establish a successful due diligence defence.

c) Reg. 308-Emission

Section 9 of Regulation 308 governs air emissions from stationary sources of air pollution. Where emission of air contaminants exceeding in quantity or concentration those prescribed by regulation (including those causing any of the adverse effects specified in s. 6) results from

1. failure to operate in the normal manner;

2. change in operating conditions; or

3. shut-down of the source or any part thereof

notification must be given by the owner or operator of the source of air pollution.

2. CEPA - Release

Section 36 of CEPA creates reporting and emergency notification duties where a release occurs or where there is a reasonable likelihood of a release into the environment of a toxic substance in contravention of the regulations. "Release" includes "discharge, spray, eject, inoculate, abandon, deposit, spill, leak, seep, pour, emit, empty, throw, dump, place and exhaust".

Section 57(1) imposes corresponding obligations in respect of substances designated by regulation (under Section 54), relating to federal works, undertakings or lands. For example, 50R/90-5 regulates mobile PCB treatment and destruction on federal lands or under contract with federal institutions.

Currently there are 13 classes of chemicals designated as toxic on Schedule I. Generally, regulations have been enacted to control or prohibit their use and release.

IV. STATUTORY REPORTING OBLIGATIONS: WHO MUST BE NOTIFIED; WHAT MUST THEY BE TOLD

A. EPA

1. Discharge

Section 15(1) imposes an onus on an individual who discharges, causes or permits a discharge of a contaminant "our of the normal course of events that causes or is likely to cause an adverse effect" to "forthwith" notify the Ministry of the Environment.

Section 13(1) requires the giving of notice to the Ministry of all discharges of contaminants that exceed regulated standards or which may cause an adverse effect. The s. 13(1) obligation applies only to persons who discharge the contaminant or to persons responsible for the source of the contaminant.

The statute does not require reporting of any specific information. The person notifying the Ministry or Spills Action Centre (SAC) should describe the specific location of the discharge, the general nature of the discharge and specific information which will allow the Ministry or SAC to notify appropriate emergency response agencies. No information need be given about the cause of the discharge, nor the identity of the person or persons causing or permitting it.

2. Spill

Section 92(1) requires every person who has control of a pollutant that is spilled and every person who spills or causes or permits a spill of a pollutant that causes or is likely to cause an adverse effect to notify forthwith

i) the Ministry of the Environment;

ii) the regional municipality where applicable, otherwise the local municipality;

iii) the owner of the pollutant; and

iv) the person having control of the pollutant.

Notification made pursuant to this section must include the circumstances of the spill and the action the person has taken or intends to take respecting the spill. The person giving the report is not obliged to disclose the cause of the spill nor the identity of the person causing or permitting it.

Section 92(2) provides that the duty to report comes into effect "immediately he knows or ought to know that the pollutant is spilled and is causing or is likely to cause an adverse effect". This wording implies that a person could be convicted for failing to report a spill even though he was not aware of it. The phrase "ought to know" implies that a person whose business activities may result in a spill should take precautions to ensure that all spills are detected and reported promptly. Failure to do so may result in a breach of this statutory duty and in prosecution.

Section 92(4) requires police officers and municipal and public employees who are informed of or investigate spills to report them to the Ministry.

B. EPA AIR EMISSIONS - REGULATION 308

Notification must be given by the owner or operator of a stationary source of air pollution where excess emissions result from a process upset or shut-down of equipment.

Notice must be given to a provincial officer

- i) immediately of the particulars of the failure, change or shutdown; and
- ii) as soon as practicable in writing giving the particulars of the failure, change or shutdown.

This notice is most often given to local Ministry of the Environment abatement officers rather than the Spills Action Centre (described below).

C. MUNICIPAL SEWER-USE BY-LAWS

Most sewer-use by-laws provide that every person who discharges or deposits, or causes or permits the discharge or deposit of the material which must be reported that person must forthwith notify the municipality in which the discharge took place and the area municipality receiving the discharge or managing the land drainage works or storm sewers.

The notification must include the following information:

1. name of the person and address of the location of the spill;

2. name of the person reporting the spill and telephone number where that person can be reached;

3. time of the spill;

4. type and volume of material spilled; and

5. corrective actions being taken to control the spill.

In addition to the immediate notification requirement, most sewer-use by-laws provide that a detailed report must be submitted within 5 days following the discharge or deposit to both the municipality and area municipality. For example, if the spill took place in the City of Etobicoke the report would be made to Etobicoke and Metropolitan Toronto. Etobicoke has a sewer-use by-law based on the provincial model as is that of Metropolitan Toronto.

This detailed report usually is to be in and writing and usually must describe the cause of the spill and actions taken or to be taken to prevent a recurrence. While it is unlikely that the information given regarding the cause of the discharge can be used against the person causing or permitting it in a prosecution, (see the discussion infra of R. v. Weil's Food Processing) the written report should be carefully prepared. It is prudent to have a report reviewed by legal counsel before submitting it.

D. CEPA

Section 36 requires any person who

i) owns or has charge of a substance immediately before its release or likely release; or

ii) causes or contributes to the initial release or increases the likelihood of the initial release

to report the matter as soon as possible in the circumstances to an inspector or other person designated by regulation. The person required to report must also make a reasonable effort to notify any member of the public who may be adversely affected by the release or likely release.

Section 36(4), noted below, permits designation of provincial officials to receive reports.

E. SPILLS ACTION CENTRE

In Ontario an effort has been made to coordinate the reporting of spills between federal, provincial and municipal governments and to ensure appropriate reporting and response by agencies at every level of authority.

The Spills Action Centre often coordinates the reporting of and response to spills, whether "routine" or emergency.

Spills may be reported directly to the Spills Action Centre which is staffed around the clock. Staff members are trained to advise on the nature of the reporting obligations and may undertake to notify the appropriate federal, provincial and municipal agencies as required. They may contact appropriate emergency response organizations at various levels of government, from police, fire, ambulance and public works to provincial and federal environment officials. They may also contact other potentially affected parties and agencies including the Coast Guard and U.S. authorities. The Spills Action Centre has 24 hour access to the Minister of the Environment.

The Canadian Environmental Protection Act, (CEPA), S.36(4), provides that if a province has provisions in force for dealing with a release of toxic substances the Governor General can make regulations allowing the mandatory report to be made to the "person designated by the provincial provisions." Regulations under this section are not yet in force.

The staff at the Spills Action Centre has stated that it reports spills to federal officials in the appropriate cases.

British Columbia's Provincial Emergency Program, corresponding to Ontario's Spills Action Centre, forwards all reports to Environment Canada.

V. FAILURE TO REPORT

A. PENALTIES

1. EPA

An individual who fails to report under sections 13(1), 15(1) or 92(1) is subject to a fine of not more than $10,000 on first offence and $25,000 on subsequent offences. (s. 186(5))

Fines for a corporation convicted of this offence range from a maximum of $50,000 on first conviction to a maximum of $100,000 on second and subsequent convictions. (s. 186(6))

2. Municipal Sewer-Use By-laws

The Municipal Act authorizes maximum fines for corporations of $50,000 per day on first offence and $100,000 per day for subsequent convictions. Individuals are liable to maximum fines of $10,000 and $25,000 per day respectively. These fines are adopted in most sewer-use by-laws.

As noted above, in many cases an investigation or prosecution under the sewer-use by-law may be followed by an investigation and subsequent charge under provincial legislation as well.

3. CEPA

Every person who fails to make a report under section 36 is subject to a maximum fine on summary conviction of $300,000 and up to 6 months in jail. On indictment the maximum fine is one million dollars and a jail term of up to three years.
(S.113)

B. LIABILITY OF OFFICERS AND DIRECTORS AND EMPLOYEES

1. Ontario

Directors, officers and employees may be liable for failure to report a spill or discharge if they were responsible for causing or permitting it. As noted above, the fines for individuals convicted of failure to report can be quite significant.

In R. v. Hill (unreported, May 24, 1988, Ont. Dist. Ct., aff'd June 26, 1988, Ont.C.A.) a Texaco area supervisor failed to report a spill or send a clean-up contractor for 11 days. He was convicted of failing to report for each of the 11 days that the spill remained unreported.

A consultant who is aware of a discharge or spill and fails to report it may found to be a party to the offence under the Provincial Offences

Act[3].(s.77. Note that s.78 prohibits counselling or procuring another person to be a party to an offence.) Engineers are subject to a statutory Code of Professional Conduct and Code of Ethics which requires disclosure where public safety is at risk.

Directors and officers of corporations engaging in activities that may result in discharges are also subject to a statutory duty to take all reasonable care to prevent the corporation from causing or permitting an unlawful discharge. Failure to carry out that duty is an offence. (s.194)

In R. v. Bata Industries Limited[4] two corporate directors were convicted under the Ontario Water Resources Act in relation to pollution caused from improper storage of waste which contaminated the soil and groundwater around the industrial premises. Each director was fined $12,000 and the judge prohibited the company from indemnifying the directors for the fines.

The standard of behaviour required to avoid conviction is that of due diligence. It is not necessary that the offence occurred intentionally; if the directors, officers or corporate agents were negligent, they may be convicted.

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[3] R.S.O. 1990, c. P-33

[4] (unreported decision of Ormston J. (Ontario Court (Provincial Division), February 1, 1992, sentencing decision released April 6, 1992)

2. Municipal Sewer-Use By-laws

Individuals and corporations both are generally obliged to comply with sewer-use by-laws. Failure to do so may result in charges being preferred against the individuals breaching the by-law and the corporation.

Although it is not usual for municipal officials to charge individuals for failing to report a corporate discharge, repeated violations of a sewer-use by-law have resulted in serious consequences for a company president.

In R. v. B.E.S.T. Plating Shoppe Ltd. (1987), 1 C.E.L.R. (N.S.) 145 a company which had repeatedly been convicted violating the sewer-use by-law was charged with contempt for violating a court order prohibiting discharge of plating waste in contravention of the by-law. The president of the company was also charged personally.

On the president's appeal from a six month jail sentence, the Court upheld the jail term (Municipality of Metropolitan Toronto v. Siapao (1988) 3 C.E.L.R. (N.S.) 122) The president of the company had control of its operations, was aware of pollution it was causing and understood how the pollution could be controlled. He took no significant action to attempt to control the pollution and was, therefore, in contempt of the order prohibiting the company from violating the sewer-use by-law.

3. CEPA

Section 122 provides that an officer, director or agent of a company that commits a CEPA offence is a party to and guilty of the offence if he directed, authorized, assented to, acquiesced in or participated in the commission of the offence.

VI. THE REPORTING DILEMMA

A. THE CHARTER OF RIGHTS AND DUTY TO REPORT

It has become imperative for Ontario companies to establish spill response and reporting programs for complying with Part X (formerly Part IX) of the EPA. It is difficult for every employee to know the law or understand what is a minor event and what must be reported to government agencies. The rule of thumb in some workplaces is "if you have to wipe it up then its a spill". Employees are instructed to report every incident to the person in charge of spill response, who in turn must decide whether or not further action must be taken.

Ontario's Minister of the Environment has stated that:

> Strict reporting requirements and increased enforcement have convinced industry that it is in its best interests to report all spills.[5]

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[5] Ministry of the Environment News Release, February 22, 1991.

One result has been the increase in reporting of spills since 1986 by about 20% each year. 5,345 spills were reported in Ontario in 1989, according to a report release in March of 1991 by Ontario's Spills Action Centre. Of these, approximately one-third were spills of less than 10 litres. Approximately one-half of all reported spills involved oil or fuel.[6]

Emphasis by the MOE on enforcement rather than abatement may foster reluctance to report. In many cases, without a report, the Ministry would have no knowledge of a given incident, that is, nothing on which to base a charge for a pollution offence. Since pollution offences carry greater fines for subsequent convictions and require costly legal defence, some managers argue in favour of reporting only larger more visible events as spills.

The 1991 Ontario General Division decision in the case of R. v. Weil's Food Processing Ltd. and Henry Weil (unreported 2 part decision of Browne J. released December 4, 1990 and September 20, 1991) has recognized the dilemma facing those who are involved in what may later be determined to be a "spill". The judgement considered whether the mandatory reporting requirements of EPA s.14(1) (now 15(1)) and s. 16(2) (now s.30(2)) of the Ontario Water Resources Act violate the principle of the right to silence provided by the Canadian Charter of Rights and Freedoms. Mr. Justice Brown stated:

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[6] Ministry of the Environment News Release, February 22, 1991. Distribution of spills among industrial sectors reporting was: transportation -13.4%, petroleum-13.3%, chemical-10.9%, metallurgical -9.4%, and electric utilities-10.6%. Sewage treatment plants, other industrial, agricultural and residential sources accounted for less than 5% each.

> It is a desirable goal that notice be required and that failure to give notice be an absolute liability offence. I find it surprising that the legislation requiring the giving of notice does not provide further that the compliance would not be admissible against a party giving the notice. As the legislation now stands the giving of notice would not be a neutral fact. The giving of the notice and the particulars given would almost certainly be elements in establishing other offences. What does the citizen do? If they fail to give notice, that is an absolute liability offence. If notice is given, it may be used against the interest of the giver. The goal of seeking the giving of notice is frustrated by the built-in conflict....I conclude there is a clear infringement of s. 7 of the Charter subject to any relief that may be available pursuant to subsection 1.

In late June of 1991 the court heard argument on whether section 1 of the Charter applied to the reporting requirements. Section 1 guarantees Charter rights subject to "such reasonable limits prescribed by law as can be demonstrably justified in a free and democratic society".

Judge Browne decided that the mandatory reporting provisions in the EPA and OWRA did offend the Charter, but that the sections should be "read down" so as to prevent use of the report in a prosecution as direct evidence against the person making the report.

The decision states:

> As the sections are unconstitutional only to the extent that the notice can be used in proceedings against the giver of the notice,
>
> the sections should be interpreted as providing that the notice not be used against the giver.

It is interesting to note that the Crown tendered evidence that no individual who reported a spill in has been personally charged with an offence related to the spill (although that person's corporate employer may have been charged).

The Weil's Food Processing decision was followed in the recent Bata Industries case (unreported Provincial Division decision of Ormston J. released February 7, 1992).

British Columbia's mandatory spill reporting legislation, like that of Ontario, does not provide that information reported may not be used in the prosecution. It is likely that the Weil's Food Processing decision will apply to charges in BC as well.

B. WHAT TO REPORT

1. The Law

The Weil's Food Processing decision leaves open the question of derivative evidence. That is, if the prosecutor only discovers an event from information provided through a mandatory report, will evidence derived from an investigation based on that report be admissible?

Also before the courts is the issue of whether a defendant who reports more information than is required by the law is subject to having that information used against him in his prosecution.

A company filed mandatory spill reports with the Spills Action Centre for a number discharges of chemicals. In the reports the company described the actions it had taken to prevent the spills. The Crown contended that these actions were not sufficient to establish the degree of due diligence required to constitute a defence to the charges.

The EPA requires that a person who must report a spill provide the following information:

1. the circumstances of the spill; and

2. the action that the person has taken or intends to take. (s. 92(1)).

The Director may require additional information regarding the "pollutant, the source of the pollutant and the spill of the pollutant" (s. 92(3). By the principle in the Weil's case, such information, given under compulsion would not likely be admitted as evidence in the prosecution.

Where the accused company voluntarily supplies such information, either in error, or to try to establish to the Ministry that it took all precautions and should not, therefore, be charged, the Crown contends that this information is admissible. Since the specific information the Crown wished to rely on was not given under compulsion (that is, although the EPA required some information, it did not require that specific information), the Crown argues that it is admissible evidence. The company admitted the spill, and therefore the spill report was not needed to prove the actual offence.

Therefore, in this case, the Crown is not seeking to use the report to prove the offence, but to prove that the company did not use all reasonable means to prevent the spill, on its own admission.[7]

Apparently the company used the same spill report form for both internal purposes and for reporting to the Ministry of the Environment. Instead of having a separate form for Ministry reporting purposes, the company inadvertently provided the Ministry with information it now wants to exclude as evidence in the prosecution.

The decision in this case is expected this summer.

2. The Practice

Environmental managers who wish to comply with the law without inviting extra liability should ensure that, as part of the spill response and reporting program, reporting is done wherever possible by supervisory individuals who have been trained to do so.

Those making reports should be clear about what information must be given. It is important to stick to facts known to the person reporting. He or she should not discuss the cause of the spill. Sources of information should be made clear if not based on firsthand knowledge. Speculation should be discouraged.

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[7] An interesting sidelight to this case is that the company rated among the most frequent reporters of discharges in a recently released report on provincial spill statistics.

A record of all of the details of a telephone report to any government officials or agencies should be kept. Those reporting spills should be aware that the Spills Action Centre records all calls. Therefore a careful log of what is reported is important.

Many companies use spill report forms which must be filled out by anyone witnessing a spill. The form is filled out as soon as possible and given to person in charge of spill reporting, who determines whether the event is reportable. He or she may then use another form for the purpose of reporting the spill which will show all the categories of information that the company has determined are in keeping with the practice of its industry for spill reporting.

C. WHEN TO REPORT

Spill reports should be made as soon as possible after the event occurs. Emergency measures to protect worker health and safety take precedence over the obligation to report. In some circumstances it will be more pressing to take emergency steps to stop the escape of the pollutant or to take measures to contain it than to take the time to report it. A spill response and reporting program should acknowledge the reasons for immediate reporting. "The immediate concern of the MOE and others is with evaluating whether a spill/release may endanger the public and thus they must clearly understand the magnitude of the situation."[8]

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[8] "Shift Superintendent Guide To Forthwith Reporting of Spills/Releases To Government Agencies", Esso Petroleum Canada and Esso Chemical Canada Sarnia Site (January 9, 1990), from the court record in Weil's Food Processing

D. PROOF OF FAILURE TO REPORT

In the Bata decision[9] the defendants were charged with failing to report discharges. The Crown attempted to prove that the defendant failed to report by filing a certificate indicating that a search of the Spills Action Centre database failed to disclose a record of any discharge report from the defendant. The provisions of both the Environmental Protection Act and the Ontario Water Resources Act, on which the charges were based, require reporting to the Ministry and Minister of the Environment respectively.

In the circumstances in Bata, where the discharge came from leaking barrels improperly stored on site for several years the judge was satisfied that the pollution did not result from a "spill" as defined in the Environmental Protection Act. Therefore, proof that the defendant had not reported the discharges to the Spills Action Centre did not satisfy the onus of the Crown to prove that the defendant had failed to report a discharge of a contaminant out of the normal course of events.

This technical distinction permitted the judge to find the defendant not guilty of the offence of failing to report.

In Ontario it appears that it may be difficult for the Ministry to prove that a spill was not reported, since the duty to report to the Ministry as provided in the Environmental Protection Act does not specifically require reporting to the Spills Action Centre. It remains to be seen whether the Ministry will have difficulty proving failure to report, since it may have to prove that no report was filed with district or regional

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[9] supra, note 4

Ministry offices, or even local sewage treatment plants which are, in many jurisdictions, run by the Ministry.

VII. CONCLUSION

The most important aspect of spill reporting is spill prevention.

A company that takes all reasonable measures to prevent spills, documents its precautions and has a carefully planned response and report program can prove to the court that it has been duly diligent. Environmental offences, including failure to report spills, are offences of strict liability, and a defendant who can persuade the court that he took all reasonable care to avoid committing the offence (i.e. that he was duly diligent) has a good defence to the charge. Sound and diligent management practices, therefore, can prevent both spills and convictions.

Cornerstones of a sound spill response program are:

1. a well designed and site specific program that provides for specific contingencies (i.e. what to do when specific substances spill);

2. a clear chain of command and instructions as to who to notify in all reasonable contingencies;

3. well trained employees who understand what to do, where to find equipment and information and how to use it in order to minimize danger and prevent damage;

4. proper, clearly established reporting procedures and responsibilities; and

5. an ongoing implementation program to ensure that everyone complies with these policies and that potential problems and weaknesses are reported to management who must act directly to correct them.

It is prudent to review the spill response plans of industry leaders and the appropriate industry associations, the provincial emergency response program and the Canadian Standards Association standards for Emergency Planning for Industry when preparing or upgrading a corporate program.

The courts will evaluate a company's defence of due diligence based on whether the company's policies and performance meet or exceed the industry standard. Conscientious environmental management and environmental policies will assist in loss prevention and may reduce or avoid the costs of defending against an environmental prosecution.

Study of Person-Portable Instrumentation for Hazardous Material Detection- Application to Chemical Spill Response

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Introduction

The Emergencies Science Division of Environment Canada has developed a priority list of potential contaminants in a chemical spill situation. The Level II Spill Response Program deals with person-portable instrumentation and is most concerned with the top 150 compounds on the Spill Priority List. The objective of that program is to develop and build a system which would enable a spill responder to measure the levels of contamination of any of these top 150 contaminants using person-portable instrumentation. Many products currently available commercially are capable of detecting one or more of these compounds. We report here on a study of such instrumentation in order to determine whether this goal can be reached and,if not, what are the areas that require further instrument development.

The present study is limited to instruments that offer the maximum potential for use within the Spill Response Program. Basic parameters include climatic compatibility, ease of use and maintenance, data manipulation features, as well as accuracy and repeatability of results and investigation of possible interferences. The study was performed under controlled conditions and according to a set protocol. Each instrument was tested within the limitations set out by the manufacturer. Manufacturers and/or distributors were approached to provide the selected instrumentation for testing over a one-week period.

The conditions which must be considered are varied, as are the characteristics of potentially spilled chemicals. Samples can be collected in the form of a gas, a liquid, or a solid; in most cases, the analyte is a contaminant in air, water, or soil. Severe environmental factors present at the spill site affect directly the use and effectiveness of the instrument. Furthermore, the operation of the instrument might have to take place while the responder is in a totally encapsulated suit that greatly hinders and limits his/her manual dexterity. These spills can occur anytime, anywhere, and the response team must be able to transport the response tools to the "hot spots".

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History

This study builds on information compiled in other projects. For example, an instrument review (1989) and the Chemical Spill Priority List (1990) are the two major references to this work.

The former instrument review was published as Environment Canada publication EE-118 and reported information on over 200 instruments. The criteria for that review were: the detection of one or more compounds on the spill priority list (1980); availability in Canada; and to be person-portable. The report contained information supplied by manufacturers and distributors and no formal in-house testing was performed. The instruments covered in EE-118 were used as a starting point for determining which instruments would be included in this study. Development in the detection instrumentation industry led to the introduction of several instruments since the publication of EE-118. Many of these new models, however, are derived from previously existing instruments and are updates using the latest technologies.

In any portable system, there is a limit as to the amount of equipment which can be carried to and handled at the spill site. Each response group faces limitations in terms of requirements, manpower, skill, and budget. We have chosen the top 150 compounds from the Spill Priority List as the desired capability of the Level II (person-portable) spill response system. These compounds are termed primary detection capabilities. Some of the instruments chosen also detect other compounds (such as those listed in the top 250 list) which are listed under the heading of secondary detection capabilities. Many of the instruments chosen for this study are able to detect multiple compounds from the Spill Priority List. Others were chosen because of their ability to detect a single high-priority compound which does not fall into a traditional compound "family".

Standardized Test Parameters

Portability

Portability is not easily defined. The concept is subjective, pertaining to the user's physical attributes and also the conditions for use. For a Level II response system, the instrument should be able to be carried in no more than one hand. This is a reasonable condition. In this way, the responder is able to keep one hand free for a variety of anticipated tasks (e.g. opening doors, adjusting airflow on SCBA, or support while climbing).

Dimensions and weight are both obvious portability limitations. If more than one dimension is greater than 8 cm, the instrument should have some sort of handle or strap. Some instruments are equipped with sufficient straps for hands-free operation. Any instrument which is designed to be carried in one hand should not exceed 12 kg. Instruments heavier than this may still be considered person-portable if equipped with a backpack carrier, otherwise they are considered luggable and can at best be carried between locations for short distances only. The backpack carrier option is impossible when the responder is using a SCBA.

Another portability limitation is power supply. AC powered instruments are better suited to a semi-permanent location, even if they are touted as portable. As for battery-powered instruments, the power may be supplied by alkaline, rechargeable NiCad, or rechargeable lead-acid batteries; all types have their merits and disadvantages. For spill response purposes, a four- hour minimum service should be provided. A longer battery life not only allows for a longer service period, but also provides for a greater confidence in data recorded over an extended period. Batteries which are worn down often cause fluctuations in the operation of the instrument.

Other aspects of portability are more difficult to measure. For one, the ruggedness or field-worthiness of the instrument determines whether the instrument is suited to unfriendly conditions. THe serviceability of the instrument is greatly limited if it requires a level surface for proper operation. A waterproof casing will provide greater protection for the instrument. An RFI/EMI-shielded and/or intrinsically safe casing is an advantage, as it allows for deployment in more areas. Included as part of the instrument assessment, support materials, such as reagents or calibration gases, must also be considered.

Multi-Compound Detection

Generally speaking, as the detection capability increases, the instrument cost also increases. However, this increased cost is often offset by a reduced number of instruments required for the response system. Fewer instruments imply less service time, less training, and a more easily stored system. Several non-specific instruments can be useful, provided they can be calibrated to specific compounds. In 95% of recorded spills, there is a single, known contaminant. The most important task of the portable instrument is to provide the concentration of the known contaminant. If the instrument is able to detect multiple compounds while maintaining a reasonable degree of accuracy (±30%), then the feature is worthwhile. Instruments which are adaptable by the user for the determination of a variety of compounds are especially useful, in that they can be set up specifically for the required analyses. When preparing for a spill of any of 150 compounds, it must be anticipated that any of several instruments will be required. To be reasonable, this number of instruments should not exceed 20. With this in mind, all instruments included in this study were able to detect more than 3 compounds of interest, with the exception of the PCB analysis instruments which were nonetheless incorporated in view of the unique characteristics and the high priority ranking of these analytes.

Data Handling and Storage

In an emergency situation, the most important value is the real-time concentration. With this information, the responder can make an initial assessment of the severity of the spill. An alarm that is triggered when a pre-set level is exceeded is a definite asset. Also beneficial are peak levels and STEL for hazardous gases and vapours. These levels help to determine the safety risk to the responder. Other benefits to assess are stored calibration values and data storage. Those instruments which have data storage should provide the capability to store date, time, and location code alongside the raw data.

Facility of Use

The level of knowledge, abilities and training of each responder varies greatly, consequently a "user-friendly" instrument is a must. Instruments with numerous functions should have menu-driven and/or step-through functions. This will assist the user to apply the correct set-up and also to increase the user's confidence level. The emergency situation is stressful and any way to alleviate that pressure is advantageous.

The physical manipulation of the controls is also important. In the event that the responder is in a fully-encapsulated suit, the operation of the instrument becomes significantly more tedious. The key grouping as well as the type of controls and the labelling are important.

Interpreting the resulting data is the next challenge. The meter must provide easy-to-read figures in both bright and dim light. When possible, the units should be presented alongside the numerical value.

All of these advantages are enhanced by a proper training routine. Refresher courses should be undertaken as a follow-up to initial instrument training. Increased familiarity produces efficiency of time and effort in a response situation.

Rapidity

The ability for an instrument to provide results quickly can be measured in many ways. For one, the response time can be measured as the average time taken to reach a steady value after a contaminated sample is introduced. The recovery time, namely the time required to return to background levels once a contaminant which has been at alarm concentration has been removed, is of importance. The initial response time is measured from the point when the instrument arrives on site to the point where the first results are reported. Arriving on site implies that the instrument would be in a state suitable for storage in transport. Some instruments should be calibrated on-site. In this case, the calibration time is also important. All of these factors should be considered in a first-response scenario.

Environment

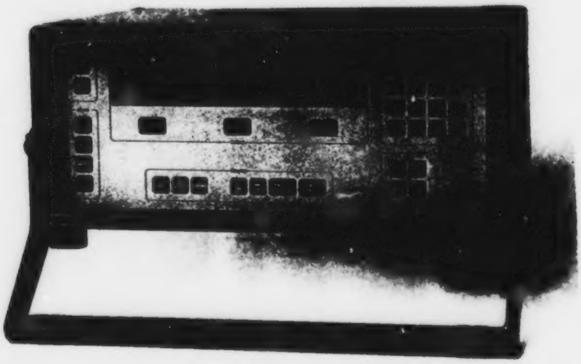
The ability of the instrument to overcome environmental changes is important, since the potential ranges of conditions are widespread. The temperatures encountered by a spill responder are typically in the range of -25C to +30C, although -15C to +25C is the most likely. The relative humidity is normally between 10% and 90%. Instrumentation should be useful over these ranges, where possible. In air and water testing instruments, there should be some consideration for high particulate levels in the sample. Different water and soil types should be accommodated by the related testing procedures.

Response by the instrument should be tested at both elevated and depressed temperatures, relative to the temperature at which it was calibrated, in order to compare results. We also anticipate that an instrument may be transported and stored at ambient temperatures below the normal operating range. In this case, the time required to commence operation after storage at -10C is a useful measurement.

Applications

Several examples of instrumentation which has been tested are presented in the following pages. On completion of instrument testing, a comprehensive report will be issued through Environment Canada.

Model 1302 Multi-gas Monitor



This is an infra-red detector used for low-level detection of various gases in air. The instrument holds a bank of six discreet wavelength filters for detection of certain compound groups. A sample is drawn into the sample chamber through the use of an internal pump. Full analysis requires less than two minutes, followed by a purge of the sample cell and introduction of the next sample. The instrument is enclosed in a water-resistant, hard-plastic shell. Data gathered can be manipulated, processed, and stored.

Portability

Dimensions (HWD, cm)	17.5 x 39.5 x 30
Weight	9 kg + 9 kg battery pack
Carrying Options	adjustable handle, backpack for DC
Power Supply	AC, rechargeable 24V DC (8hr)
Required Accessories	Battery charger

Operation

Controls	Logic/Numeric touchpad menu-driven
Display	2 x 40 character LED
Skill Level Required	Advanced
Data Characteristics	last response from each filter, peak, mean, standard deviation
Data Storage	10,000 data points, raw data and alarm conditions

Performance Data

Initial Response Time	<5 min
Average Response Time	105 seconds when 6 filters in use
Recovery Time	immediate
Calibration Time	15 min
Calibration Frequency	yearly
Operating Conditions	+5C to +40C 0-90% RH
Start-up Time (-10C)	approx. 30 minutes

Primary Detection Capabilities

Compound	Range	Conc. Sampled	Accuracy
Methanol	0.04-4000 ppm	35 ppm	36.1,36.3,36.4
Sulfur Dioxide	0.3-30000 ppm	6.52 ppm	6.48,6.62,6.69
Toluene	0.04-4000 ppm	80 ppm	82,82,80
Methane	0.1-10000 ppm	498 ppm	490,497,495

Similar values are anticipated for the following gases:

Acetic acid
Acetic anhydride
Acetone
Acetylene
Acrylonitrile
Ammonia
Aniline
Benzene
Butyl alcohol
Carbon tetrachloride
Cresol
Cyclohexane
Diethylamine
Dimethylamine
Ethyl alcohol
Ethyl chloride
Ethylbenzene
Ethylene
Ethylene dichloride
Ethylene oxide
Formaldehyde
Formic acid
Hexane
Hydrazine
Isopropyl alcohol
Methyl chloride
Methyl ethyl ketone
Methyl methacrylate
Methylene chloride
Perchloroethylene
Phenol
Propylene oxide
Pyridine
Styrene
Trichloroethane
Trichloroethylene
Vinyl Acetate
Vinyl Chloride
Xylenes

Other Features

Electronic calibration possible

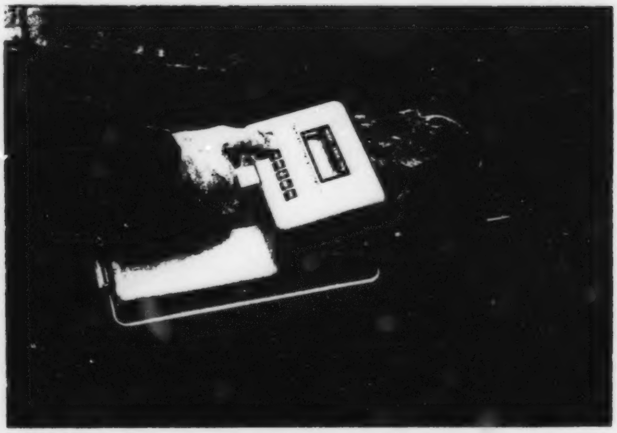
Comments

1. Sampling may be automated.
2. User must choose filters for expected application.

Commercial Information

Price Range	$ 25,000 - 30,000 + $ 2,500 - 3,000 per filter
Manufacturer	Bruel & Kjaer Canada Ltd. 7 Slack Rd., Unit 4, Ottawa, ON K2G 0B7 Tel: (613) 225-7648

580B Organic Vapor Monitor



This instrument provides general analysis of many gases and vapours in air. The principle of detection is photo-ionization. Contaminants detected include any that are ionized by a 10.6 eV lamp. This type of instrument is unable to distinguish between detected gases. An internal pump draws the sample at 500 mL per minute. The entire unit is enclosed in a hard plastic shell. The 580B provides instantaneous monitoring as well as datalogging and some data manipulation. There is a user-adjustable audible alarm.

Portability	
Dimensions (HWD, cm)	15 x 17 x 43.5 (with probe extension)
Weight	2.75 kg
Carrying Options	fixed upright handle, adj. shoulder strap
Power Supply	Rechargeable (10+ hour)
Required Accessories	Battery charger, Calibration kit
Operation	
Controls	7-key logic touchpad Scrolled screens
Display	2 x 16 character LC, backlight
Skill Level Required	Advanced
Data Characteristics	real-time values, peak, average
Data Storage	stores real time data at user-selected intervals (1 second to 100 minutes), can be displayed or dumped to printer or PC

Performance Data

Initial Response Time	< 1 minute
Average Response Time	< 3 seconds
Recovery Time	approx. 2 seconds
Calibration Time	1-2 minutes
Calibration Frequency	Daily for highest confidence
Operating Conditions	0C-40C 0-100% RH
Start-up Time (-10C)	50 minutes

Primary Detection Capabilities

Compound	Range	Conc. Sampled	Accuracy
Formaldehyde	0.1-999 ppm	2.5 ppm	2.5,2.5,2.5
Toluene	0.1-999 ppm	77 ppm	77.7,77.7,80.0
Benzene	0.1-999 ppm	48.7 ppm	50.0,50.0,51.0

Similar values are anticipated for the following gases:

- Acetic acid
- Acetic anhydride
- Acetone
- Acrylonitrile
- Ammonia
- Aniline
- Bromoform
- Butyl alcohol
- Cresol
- Cyclohexane
- Diethanolamine
- Diethylamine
- Dimethylamine
- Ethyl alcohol
- Ethylbenzene
- Ethylene dichloride
- Ethylene oxide
- Ethylhexanol
- Formic acid
- Hexane
- Hydrazine
- Isopropyl alcohol
- Methyl ethyl ketone
- Methyl methacrylate
- Methylamine
- Naphthalene
- Perchloroethylene
- Phenol
- Propylene
- Propylene glycol
- Propylene oxide
- Pyridine
- Styrene
- Vinyl Acetate
- Vinyl Chloride
- Xylenes

Commercial Information

Price Range	$ 5,500 - 6,500
Manufacturer	Thermo Environmental Instruments, Inc. 8 West Forge Parkway, Franklin, MA 02038 Tel: (508) 520-0430
Distributor	SSCAN-Grodyne 90 West Beaver Creek Rd., Richmond Hill, ON L4B 1E7 Tel: (416) 222-4111

Gastech GX-91

LEL
PPM
PPM
GASTECH
MODEL GX-91
ON OFF

This is a multi-gas detector for contaminants in air. The detection principle used is electrochemical sensors. Each instrument is able to accommodate up to four of the following sensors: Oxygen, Combustible gases, Hydrogen Sulfide, Carbon Monoxide, Sulfur Dioxide. The GX-91 has an independently-powered, hand-held pump which draws the air sample at 0.5L/min. The instrument body is stainless steel construction, while the pump is housed in a hard plastic shell. This instrument provides real-time data and also performs data logging and processing. There are adjustable, two-level audible/visible alarms for all sensors. Unit tested had O_2, Combustible, H_2S, and CO sensors.

Portability

Dimensions (HWD, cm)	17.5 x 16 x 7
Weight	2.3 kg
Carrying Options	Shoulder strap, Syn. fibre
Power Supply	Alkaline batteries (>18hr)
Required Accessories	Spare batteries

Operation

Controls	3 key logic touchpad Scrolled screens
Display	2 x 20 character LC, LED alarms, backlight
Skill Level Required	Basic
Data Characteristics	Real-time, average, peak, TWA, STEL, CLG
Data Storage	5 to 300 sec. adjustable interval for raw data must be dumped to PC or printer

Performance Data

Initial Response Time	25 s
Average Response Time	< 10 s
Recovery Time	approx. 10 s
Calibration Time	approx. 10 min
Calibration Frequency	unk.
Operating Conditions	-20C to +40C 0 to 95% RH
Start-up Time (-10C)	Operational in 10 min, sensor stabilization approx. 1 hour

Primary Detection Capabilities

Compound	Range	Conc. Sampled	Accuracy
Combustible gases	0-100% LEL		±5%
Hydrogen Sulfide	0.5-100 ppm	76 ppm	75,72,77
Carbon Monoxide	1-500 ppm	12 ppm	12.5,12,11.8
Sulfur Dioxide	0-50 ppm	untested	±5%

Secondary Detection Capabilities

Oxygen, Temperature

Other Features

Intrinsically safe Class I, Div. I, Group A,B,C,D

Resistant to Radio-frequency interference

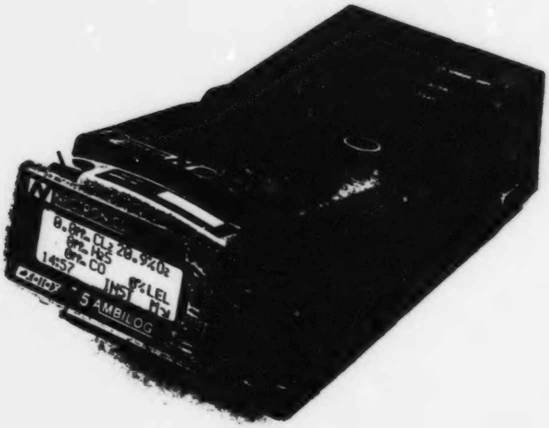
Comments

1. Performance data was accumulated using optional sampling pump. Response and recovery times may vary when not used.
2. Calibration kit available
3. Two batteries were required for the sampling pump, as well as the two required for operation of the monitor.
4. Interfering gases can affect the toxic sensors. Filters are available for improved selectivity.

Commercial Information

Price Range	$ 3,000 - 3,500
Manufacturer	GASTECH Instruments Canada Suite 146, 121 Brunel Rd., Mississauga, ON L4Z 3E9 Tel: (416) 507-8412
Distributor	Levitt-Safety 2872 Bristol Circle, Oakville, ON L6H 5T5 Tel (416) 829-2919

Exotox 75



EXOTOX® Model 75 with charger

The Exotox 75 is a five-gas detector of contaminants in air. Electrochemical sensors are used to detect Oxygen, Hydrogen Sulfide, Carbon Monoxide, Sulfur Dioxide, Chlorine, and Nitrogen Dioxide. There is also a capability to detect combustible gases. The Exotox 75 has a built-in pump which draws the air sample at approximately ⅜L per minute. The instrument is housed by a hard plastic shell. This instrument provides real-time data and can also store data. A multi-level audible/visible alarm responds to all sensors and is user-adjustable.

Portability	
Dimensions (HWD, cm)	16 x 11 x 7
Weight	1 kg
Carrying Options	waist and shoulder strap, syn. fibre
Power Supply	Rechargeable (11 hrs)
Required Accessories	Battery charger/interface
Operation	
Controls	3 key logic Scrolled screens
Display	4 x 16 character LC, backlight, LED flashing alarm
Skill Level Required	Basic
Data Characteristics	Real-time values, STEL, TWA, peak
Data Storage	sensor readings and alarm status taken at 30 second intervals, data must be dumped to PC or printer

Performance Data

Initial Response Time	20 seconds
Average Response Time	< 5 seconds
Recovery Time	< 30 seconds
Calibration Time	unk.
Calibration Frequency	6 months
Operating Conditions	-20C to +40C 0-99% RH
Start-up Time (-10C)	< 5 minutes

Primary Detection Capabilities

Compound	Range	Conc. Sampled	Accuracy
Chlorine	0.1-99.9 ppm		
Sulfur Dioxide	0.1-99.9 ppm		
Combustible gases	0-100% LEL		

Secondary Detection Capabilities

Oxygen, Hydrogen Sulfide, Nitrogen Dioxide, temperature, relative humidity

Other Features

Battery charged and logged data transferred through same connection.
Intrinsically safe, RFI protection

Commercial Information

Price Range	$ 3,000 - 3,500
Manufacturer	Neotronics of North America, Inc. P.O. Box 370, 2144 Hilton Dr. S.W., Gainesville, GA 30503-0370 Tel: (800) 535 0606
Distributor	Cantech Corporation 4119 Cousens, St. Laurent, PQ. H4S 1V6 Tel: (800) 361-6858

Conclusions

Many instruments exist with the potential to be included in a spill response system under the restrictions which have been outlined. One of the earlier questions was answered. We have defined the situations for which we are preparing the response team. We have only partially prioritized the requirements for the instrumentation. The final decisions must be borne by the response team.

This study has been undertaken for the purpose of ensuring that an Environment Canada emergency response team is adequately prepared. This information could also apply, in varying degrees, to provincial response teams, Coast Guard responders, municipal first response groups, as well as military and airport response teams, all of whom should be properly prepared for responding to their own priority compounds.

References

Fingas, M. et al, "Development of a New Chemical Spill Priority List", Proceedings of the Seventh Technical Seminar on Chemical Spills, Environment Canada, Ottawa, Ontario. 1990.

Goldthorp, M., Review of Portable Instrumentation for Field Use, Manuscript Report EE-118, Environment Canada, Ottawa, Ontario. 1989

Emergencies Response to the Grand Coulee Chemical Warehouse Fire An Analytical Aspect

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Emergencies Science Division
Environment Canada
River Road Environmental Technology Center
Ottawa

I. Synopsis

On the evening of 20 November 1991, at Grand Coulee, a small town just outside Regina a chemical transfer facility was observed to be on fire. Local firemen, knowing the nature of the fire, were instructed not to use water. They secured the perimeter and let the fire burn; at about 10 pm the fire was out. The structure, still smouldering until next morning, was totally destroyed. A large number of complaints about smoke and odour were received from as far downwind as 20 km during the fire.

The warehouse was on a private property leased by the province of Saskatchewan to store/transfer pesticides and expired chemicals from schools. In addition, cyanide salts and low-level radiation rocks for school projects were known to be present. In view of the complex and sensitive nature of the incident, assistance was sought to assess the site and to determine the degree of contamination in the vicinity.

Emergencies Science Division (ESD) responded by assembling a team of 4 scientists. The team flew out on 22 November on a special Department of National Defense flight, together with some 40 pieces of equipment and portable instrumentation weighing about one ton. On arrival, the ESD team conferred with Saskatchewan officials to work out a preliminary plan of entry and sampling program.

In the following morning, wipe samples were taken from 7 farmhouses in the vicinity of fire. At noon, preparations were taken for the initial entry. A team of two were garbed in totally encapsulated suits and with a battery of portable and radiation monitors, entered the premise the first time since the fire. A reserve team of two, similarly garbed monitored the process in case assistance was required. During the walk-around survey, a composite sample was collected for on-site cyanide analysis.

On-site monitoring revealed there was no toxic gas being release from the wrecked structure, and radiation was below concern level. There was some splattering of pesticides stored at the northeast side of the warehouse, evident from reddish coloration of the adjacent soil, as well as yellow stains on some of the remaining structures.

Once the hazard level was ascertained, subsequent entries were carried out in "C-level" gear and extensive surface sampling campaign was conducted inside the warehouse. High priority samples, consisting of house wipe samples and residue samples collected inside the warehouse were flown back to Ottawa where all lab analyses were carried out. Excess equipment was also packed up and shipped back on the same military flight. Two members remained on-scene to continue the sampling program. In all, over 200 samples were taken including surface wipes from structures and upwind/downwind locations of soil, residuals, vegetation and snow.

This paper details the analytical activities associated with samples collected on-site. The findings, their significance and discussions on methodology are included.

II. Experimental

Sampling

Wipe samples: surface contamination was recovered by using a hexane-soaked cotton swab over an area of one square meter. These samples included wipes on exterior windows of farmhouse exposed to the smoke plume, and interior floors on the side nearest the fire. Those samples received the highest priority to allay any fears the community might have. In addition, the surface of the remaining structure visibly contaminated by pesticide sprays was sampled to determine the nature of contamination.

Soil/aggregate samples: disposable scoops were used to remove the surface soil samples to an average depth of 2 cm. The soil to the north east side of the warehouse was stained a pinkish coloration. The peripheral soil was sampled systematically to determine the boundary of contamination.

A preliminary sample was taken on initial entry for cyanide determination. This was a composite sample taken around the perimeter of the remaining structure and consisted of charred pieces of the structure, surface residue and sludge.

Field Cyanide Test

A Person Portable Analytical Kit (PPAK) was used for the on-site titrimetric measurement for cyanide. A 10-gm aliquot of the composite aggregate sample was extracted with 50 ml deionised water. The supernatant was filtered through a course filter, and titrated with 0.01 M silver nitrate after the addition of 10 drops of Dimethylaminobenzylidene rhodanine. The colour change is from yellow to red due to the formation of silver cyanide complexes. The method has a useful range of 0.5-50 mg/L cyanide (ref 1). The test of the burn residue turned out be negative.

Sample Workup

Extraction

Wipe samples were soxhlet extracted in acetone for 12 hours. Extraction apparatus was blanked between runs using dichloromethane (DCM) to minimise any cross contamination. The raw extract was filtered through anhydrous sodium sulphate and concentrated by rotary-evaporation to about 3 ml. The concentrated extract was then quantitatively transferred to a graduated test tube and blown down under ultra high purity nitrogen to typically 1 ml before analysis.

Soil samples were air-dried, homogenised and a representative aliquot (typically 5 gm) was weighed and extracted by soxhlet as described.

To speed up turn around time, an ultrasonic extraction was also tried. Wipe samples were placed in a test tube and extracted in an ultrasonic bath 3 times for 10 min each in acetone. The extracts were combined, dried over sodium sulphate and concentrated to 1 ml.

Analysis

All analysis was carried out on a Hewlett-Packard (HP) 5890 GC/5971A Mass Selective Detector (MSD) equipped with a HP7673 Automated Liquid Sampler (ALS). A 25 meter HP-1 cross-linked methyl silicone fused silica column (0.2 mm id, 0.3-μm film thickness) was used to separate the complex mixture into individual components. One μl of the raw extract was injected in the splitless mode with a solvent delay of 4 min. A 386-PC loaded with HP G1034B software was used to acquire and process data.

GC Parameters

GC temp program: 50°C/min to 270°C/5 min (rate 10°C/min); then to 285°C/3 min (rate 25°C/min)
Injector temp: 250°C
Interface: 290°C, direct
Linear velocity: 50 cm/sec at 100°C
Volumetric flow: 0.7 cc/min nominal
Head pressure: 12 psi

MSD Parameters

Operation mode: linear scanning, 45-450 amu with A/D=2exp2 (1 scan/sec),threshold 100
Electron multiplier: 2000 V nominal
Source pressure: 5*10exp-5 at 100°C
Tuning: autotune

Compound Identification and Confirmation

Even though the emergency responders were extremely fortunate in this case that the chemical inventory was well known, there was no prior knowledge as to the actual concentration of pesticide in the samples. The raw extract was screened at 1 ml volume or higher to reduce the chance for irreversible contamination of the injection port, GC column or the ion source. Upon completion of the GC run, the chromatogram was integrated using the autointegration function. In this process, the threshold and peak width integration parameters were optimised. This mode of integration gave satisfactory results for most unknown chromatograms.

The next phase in data processing was to identify each peak in the chromatogram. The process was facilitated by using the autosearch function which compared all peaks against the 49,000-spectra NBS library in the data system and printed out three of the best fit compounds. Analytes of interest, eg. chlorinated pesticides, polycyclic aromatic hydrocarbons (PAH), etc. were then flagged and manually compared with published spectra. This was important as some peaks co-eluted or were of such low intensity that human interpretation was always necessary. Later on, as more samples were analyzed, retention times of known pesticides and analytes of interest in highly contaminated samples were used to establish elution windows which helped chemical identification and quantitation significantly.

Quantitation

As the first batch of top priority samples were being extracted, there was a scramble to make up standard solutions of all chemicals known to be stored in the warehouse. Standards were obtained from Supelco (Bellefonte, PA), Ultra Scientific (North Kingstown, RI), or from Polyscience (Niles, Ill). As all standards had purity of 98% minimum, they were used as received without further purification. The only exception was the pesticide,"Laser", which was available through Hoechst, a manufacturer of the chemical in Regina.
Once the analyte was positively identified, its peak area counts was compared to that of an authenticated standard and its concentration calculated (external standard method). For simplicity of reporting and ease of interpretation, the analytes were grouped into families,eg 4,4'-DDE, 4,4'-DDD, 2,4'-DDT, 4,4'-DDT etc were grouped together and reported as DDT.

Headspace Analysis of Soil Sample

A HP1939A Headspace Analyzer was coupled to a HP5890 GC/5971A MSD. A 300-series Pascal Data Station was used for system control and data processing. A 5-gm aliquot of soil was loaded in the headspace vial and equilibrated at 85°C for 30 min. A 1-CC aliquot of the headspace was injected onto the GC/MSD via a gas sampling loop. The column was a HP-1 column (25 M*0.3 mm id, 1-μm film) and the MSD was operated in scan mode.

Dioxin Samples

Dioxin analysis was performed by the Chemistry Division, River Road Environmental Technology Centre, Ottawa. Soil/solid samples were first spiked with a mixture of ^{37}Cl-labelled surrogate dioxin/furan. They were soxhlet-extracted in toluene and the extract subjected to acid/base column cleanup to remove the easily-oxidized organics. This was followed by fractionation on an basic alumina column to separate PCB, pesticides from the dioxin/furan. Sample analysis was performed on a Finnigan 4500 quadrupole GC/MS system (ref 2).

III. Results and Discussions

1. No analytes of interest were found in wipe samples taken from homes. In general, the chemicals found on floor wipes were waxy substances and household disinfectants. Window wipes had no chemicals traceable to the fire. Common components were hexachloroethane found in solvents and hexachlorophene (methylene bis-trichlorophenol) used in disinfectants.

2. The highest surface contamination was found on the wood shed adjacent to the warehouse. There were 2,4-D (16560 μg), 2,4,5-T (649 μg), Triallate (195 μg), DDD/DDT (52600 μg) per square meter of surface. In addition to chlorinated pesticides/herbicides, there were significant amounts of alkylated naphthalenes and biphenyls which undoubtedly originated from the fire. The western side of the shed (closer to the fire) had higher surface contamination than the east side, which might be the result of splattering of the chemicals during the fire (fig 1).

3. The pink soil found just outside the northeast side of the warehouse was contaminated with fairly high levels of 2,4-D (1610 μg/g), chlordane (1190 μg/g) and PAHs; the latter from the burning (fig 2).

4. There were fairly good correlation between the types of pesticides/herbicides and chemicals found in wipe, residue/ soil samples with the known inventory stored on site: the abundance of Heptachlor, 2,4-D and 2,4,5-T, Treflan, Endrin corresponded roughly to their relative amounts stored on site. We had not found any "Laser" (active ingredient bromoxynil octanoate and MCPA iso-octyl ester), nor was there any Supracide (methidathion) and Avadex (Diallate), Carbyne (or Barban,a carbamate herbicide) and Carbofurans. Their absence might be due to their complete consumption in the fire or, due to the relatively small quantity stored on site, they were below the detection limit of the methodology applied.

5. Although all samples were extracted exhaustively by soxhlet, five wipe samples were chosen to be extracted by ultrasonication. Those samples were first treated with ultrasound, then extracted a second time by normal soxhlet. Results indicated all analytes of interest were extracted quantitatively by ultrasonication (fig 3). This is hardly surprising, considering the analytes for all practical purpose were surface contaminants, and should be extracted relatively easily. In fact, soxhleting might in some cases even introduce complication by extracting

everything, including chemicals bound to the matrix, which may then require extensive cleanup before instrument analysis. Another consideration is the number of soxhlet apparatus that can be set up in a fume-hood, plus the long duty cycle (12 hr extraction and 6-8 hr blanking) which severely limits the turn-around time in case of emergencies.

For the pink soil, the ultrasonic extraction performed poorly. Only 33% of 2,4-D, 25% of Chlordane and 25% of PAH was extracted in comparison with the standard soxhlet method (fig 4). The homogenizers, which combine ultrasonic and mechanical means of extraction have been in use in some labs to extract environmental pollutants from sediment and filter media. If they could provide comparable extraction efficiency in much shorter time than soxhlet, they might prove to be a boon to emergencies responders by shortening the extraction step, which is often the most time-consuming step in the sample workup procedure.

6. On the whole, the GC/MSD analysis was satisfactory in view of the 'dirty' nature of raw extract. Blank runs had a slight background which later on was reduced to insignificant amount by introducing a high temperature burnout at the end of the temperature program. The response factors of calibration standards did not vary more than 20% during the duration of this project. We "guesstimated" the final volume of the raw extract and fortuitously, had not yet lost a GC column.

7. By comparison, the dioxin analysis was much more eventful. The pink soil from the east side of the warehouse, upon going through a multi-stage column cleanup that totalled about 14 steps, yielded a purified extract. However, at a final volume of 0.25 ml, the extract turned out to be too concentrated and the residual background material "killed" two GC columns!
None of the samples submitted for dioxin analysis (one wipe sample from inside the wood shed, one composite soil and a residue sample inside the structure and the pink soil sample) had significant levels of dioxin/furan in them: the wipe sample inside the wood shed had 2 and 13 ng/square meter of tetrachlorodibenzo-p-dioxin/furan respectively, these were well below the "safe" target level of 1-50 ng/square meter.

8. Headspace analysis has the potential of providing fast turn around time by eliminating sample preparation. In addition, because only the headspace is analyzed, it is considered a clean technique and poses much less stress on the analytical hardware. However, the method is inadequate for compounds which do not have appreciable vapour pressure. The analysis of the pink soil showed chlorinated pesticides/herbicides were not detected at all; only the more volatile naphthalene and methylnaphthalenes could be detected (fig 5).

IV. Conclusions

The site was much cleaner than expected. The burning was very thorough in the sense it left very little contaminated residue behind. The fact that water was not used helped to confine the extent of contamination to within of the property limits.

Because of the diverse nature of chemicals involved, a universal analytical cleanup scheme might not be possible, or has to be foregone for the sake of rapid turn-around time. The GC/MSD, coupled with a judicial selection of sample size and extraction procedure, proves to be invaluable by separating the complex raw extract into individual components and at the same time provided unequivocal identification of the analytes by their unique spectra. Although not recommended for routine analysis, analyzing the raw extract with minimal cleanup may, unfortunately, be the norm in episodes similar to this one because of the overwhelming time constraint.

Reference

1. Goldthorp, M.D., J.T. Ruttan and M. Townshend-Colford, A Person-Portable Analytical Dit (PPAK) for the Analysis of Organic and Inorganic Compounds in Water and Soil, Manuscript Report EE-110, Environment Canada, Ottawa, Ontario, 1989.

2. A Method for the Analysis of PCDD, PCDF and PCB in Samples from the Incineration of PCB Waste, Report EPS 1/RM/3, June 1989.

FIGURE1: Two highly contaminated samples

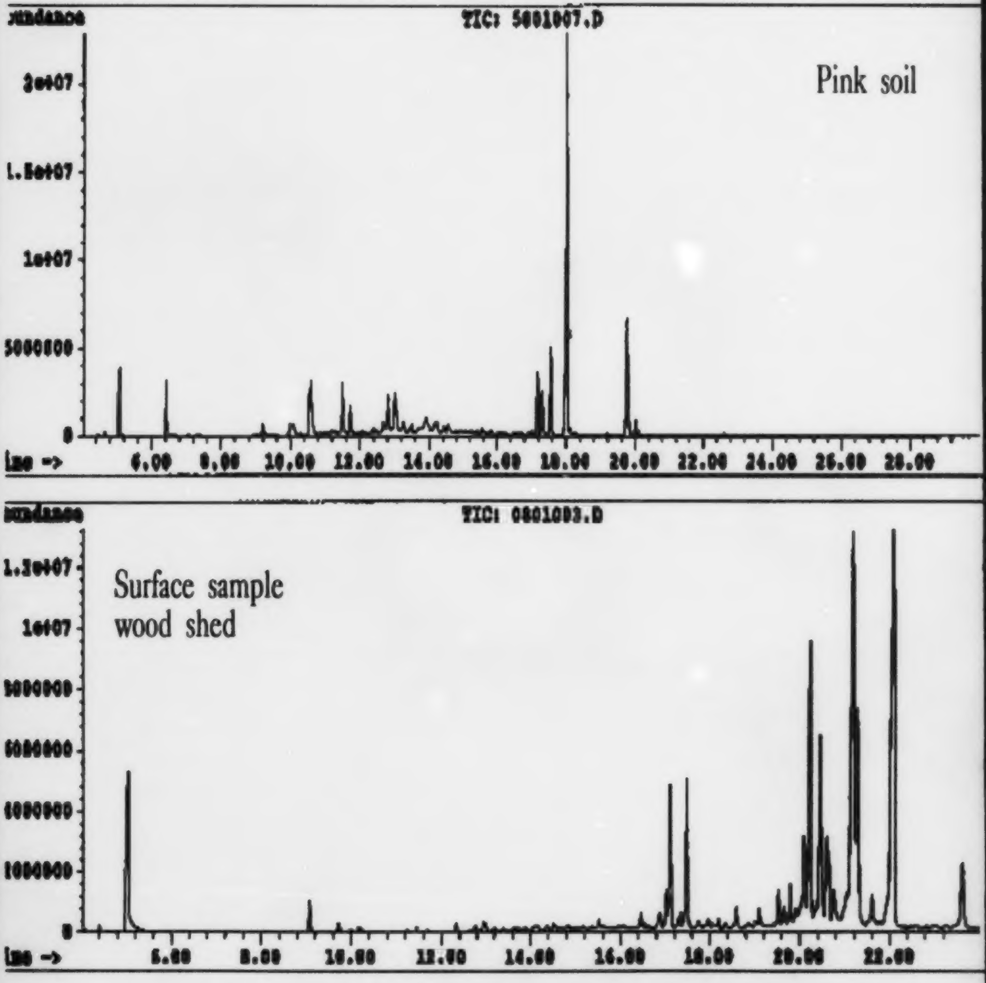


FIGURE 2: Chromatogram of pink soil

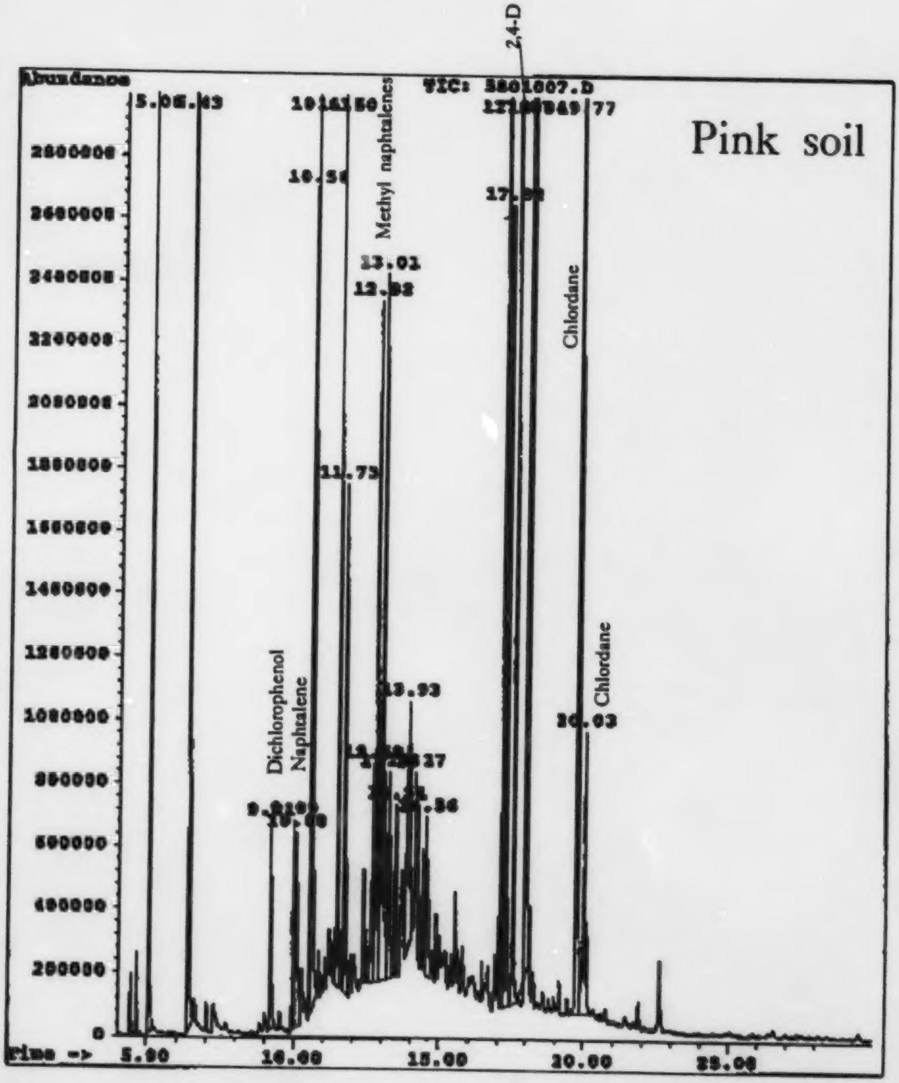


FIGURE 3: Comparison of extraction method

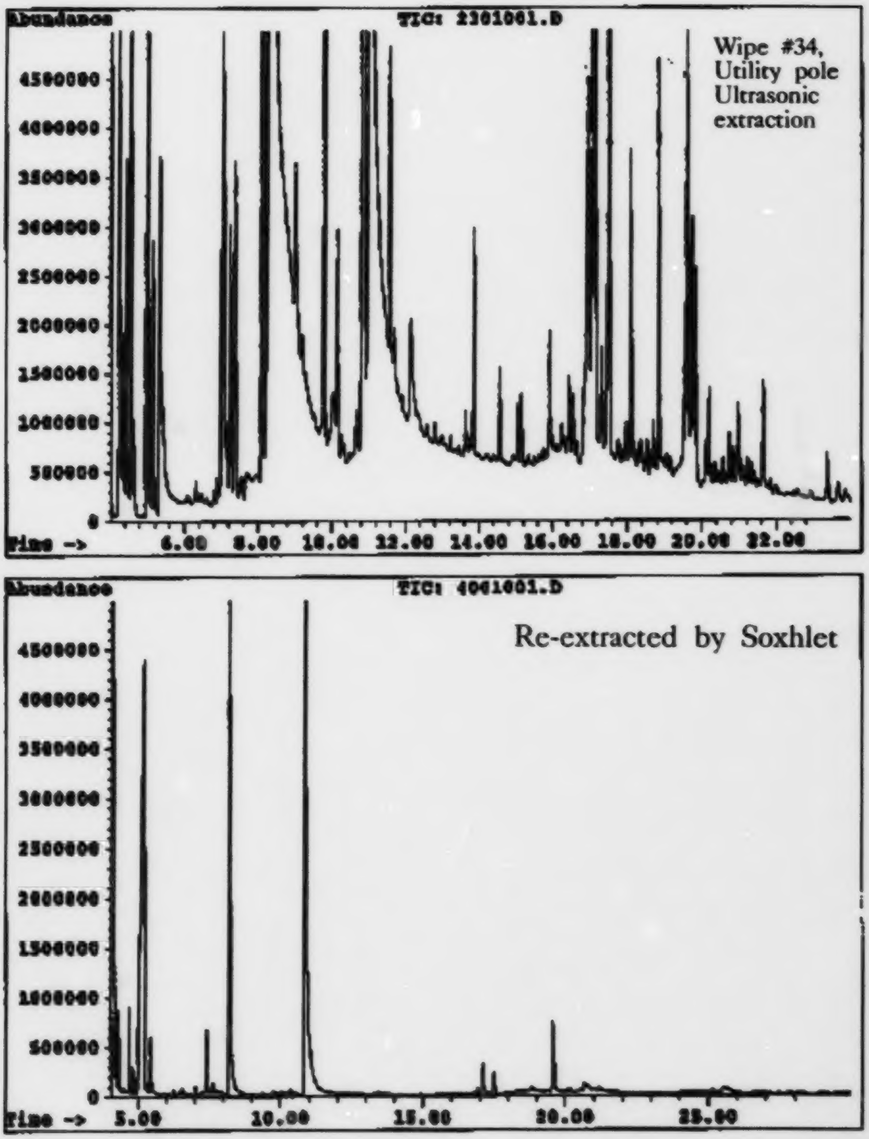


FIGURE 4: Extraction of Pink soil by various methods

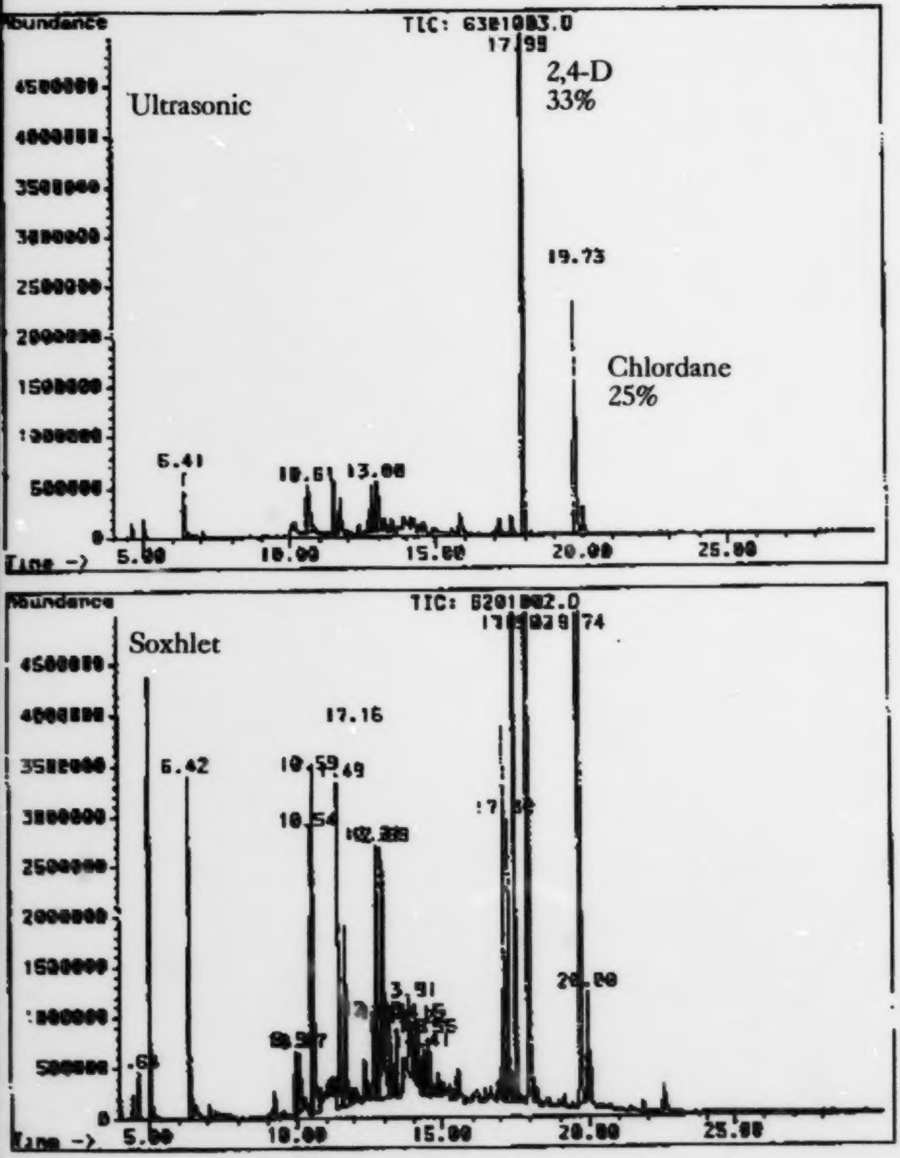
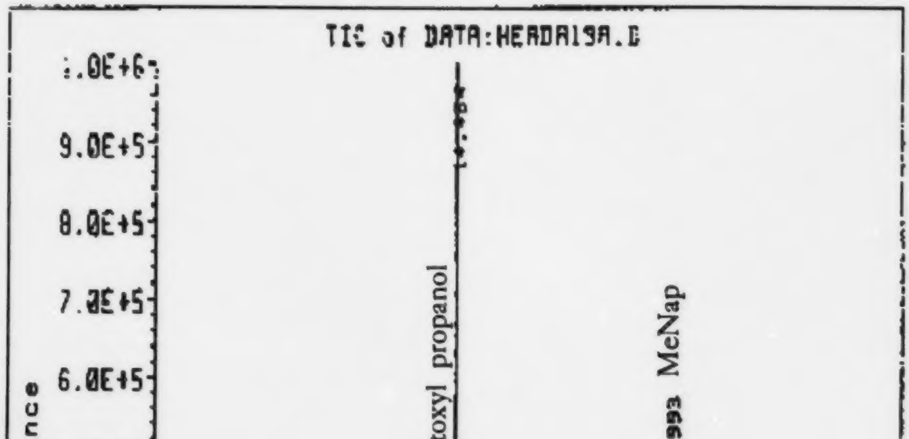


FIGURE 5: Headspace chromatogram of Pink soil equilibrated at 70 C for 30 min



REMOTE SENSING OF CHEMICALS AT SEA

by

M McDonagh, A P Payne, D Tookey
Warren Spring Laboratory, Stevenage, Hertfordshire, UK

1. INTRODUCTION

Bulk liquid chemicals are regularly transported at sea in tankers of various different sizes and design specifications. Some of these chemicals are potentially harmful to the marine environment and their transportation by sea carries with it the risk of a spill incident resulting in pollution of the sea.

Another, although less dramatic way in which chemical pollution of the sea occurs is when cargo residues, including the slops from tank cleaning operations, are discharged at sea to save the time and expense of using shore based reception facilities.

Strict conditions and limitations apply to the discharging of chemicals at sea and these are governed by the regulations in Annex II of Marpol 73/78. The needs of (a) spill management in the event of a tanker incident, and (b) of ensuring compliance with Annex II of Marpol 73/78, led to this investigation of the feasibility of using airborne remote sensing to detect chemical pollution on the sea surface.

In the UK, the Marine Pollution Control Unit (MPCU) of the Government's Department of Transport uses two light aircraft (Cessna 404 and Cessna 402) on routine remote sensing flights. They are equipped with Infra Red/Ultra Violet (IR/UV) and Side Looking Airborne Radar (SLAR) instruments to detect oil spills at sea. Instruments of these types are typical of those utilised by other countries for oil detection. Some Microwave Radiometer and Laser Fluorosensing systems are also in use but have not been evaluated here.

The aim of this investigation was to ascertain if the IR, UV and SLAR systems currently in use on the UK aircraft can detect chemicals as well as oil. The basic instrument specifications are given in Appendix A. This study was primarily concerned with chemicals that will float on sea water as the remote sensing systems respond to sea surface effects. Some soluble chemicals were also included because of interest in the ability of the instruments to assess if such a chemical is still leaking from a tanker after a spill incident.

Table 1 lists some of the main chemicals unloaded in North Sea ports together with relevant GESAMP classifications.

The IMO classification of chemicals, according to the degree of hazard they could cause to the marine environment, is prepared by "GESAMP", the Joint Group of Experts on the Scientific Aspects of Marine Pollution. Chemicals are grouped A, B, C or D in descending order of their capacity to cause damage to the marine environment.

Category A substances are the worst pollutants. Mankabady, 1986 and Kasoulides 1989 describe these as "highly hazardous to human health or aquatic life". Category B substances are "slightly to moderately toxic to aquatic life", Category C substances are "slightly toxic to aquatic life" and Category D substances are the least harmful of the four categories but still "require some attention in operational conditions".

In addition to those categorised, there are other chemicals which are listed in Annex II of MARPOL 73/78. These are chemicals which are conveyed at sea and currently considered to be harmless.

TABLE 1. - Category B, C, D Substances Unloaded in North Sea Ports

Product Name	IMO Pollution Category	Seaborne Imports (tonnes x 10^3)
Acetic acid	D	86
Acetone	-	132
Acrylonitrile	B	45
Alcohols (C_4-C_8)	D	33
Alkylbenzene	D	66
Aniline	C	49
Benzene	C	812
Butyl acetate	C	15
Chlorobenzene	B	15
Citric acid	D	30
Cyclohexane	C	227
Cyclohexanone	D	22
Dichloromethane	D	38
Dichloroethyl ether	B	18
Di(2-ethylhexyl) phthalate	-	54
Diisononyl phthalate	D	20
Dodecylbenzene	-	35
Ethyl acetate	D	30
Ethyl benzene	C	69
Ethylene dichloride	B	94
Ethylene glycol	D	70
Formaldehyde	C	12
Hydrochloric acid	D	36
Hydrogen peroxide	C	34
Isopropylbenzene	B	86
Methacrylic acid	D	44
Methylethyl ketone	-	13
Nitric acid	C	61
Octanol	C	28

TABLE 1. - Cont'd

Product Name	IMO Pollution Category	Seaborne Imports (tonnes x 10^3)
Perchloroethylene	B	17
Phenol	B	151
Phosphoric acid	D	724
Propyl alcohol	-	108
Potassium hydroxide	C	15
Sodium hydroxide	D	403
Styrene monomer	B	470
Sulphuric acid	C	466
Toluene	C	239
Trichloroethylene	B	17
Vinyl acetate	C	81
Xylenes	C	922

2. PREVIOUS WORK

There is very little published work on the remote sensing of chemicals. Sandness, 1976 describes briefly 12 different sensing techniques including thermal IR and SLAR (but not UV) before discussing their applicability to the detection of "CHRIS" chemicals, the US Coastguard's Chemical Hazards Response Information System. Little information is given regarding detection of any of the chemicals apart from identifying some theoretical considerations such as insolubility in water and low density.

The ability of airborne IR and SLAR instruments to detect dyed and undyed ethyl-2-hexanol and n-butyl methacrylate during sea trials is described by Merlin, 1991. Good quality IR imagery was obtained for the methacrylate; IR could not detect the ethyl-2-hexanol; the presence of dye had no effect. SLAR could not detect either chemical nor the diesel fuel released as a control; this failure was attributed to the relatively small sizes of the spills (1 m^3 each).

Sea trials had also been carried out previously by Warren Spring Laboratory within a trial programme in which dioctyl phthalate (DOP) and nonyl acetate were released at sea. In April 1989, 1000 l of DOP was discharged. Airborne remote sensing of the slick was provided by the Cessna 402 using Infra Red/Ultra Violet Line Scanners and SLAR. The DOP slick was easily detected by SLAR but the IR imagery was very weak to the extent that differences in grey levels were small enough to be on a par with normal variations in background readings. The DOP was not detected by the UV sensor.

In September 1989, 1000 l of DOP was discharged and imagery was obtained using the same aircraft and equipment as in the April 1989 trial. The DOP was detected by both SLAR and IR but not by UV. The IR imagery was again weak in intensity.

Similar results were obtained in July 1990 from a 1000 l discharge of DOP. Clearly, detection of the DOP using the IRLS system in the Cessna 402 has to be regarded as borderline.

During the September 1989 sea trial, 1000 l of nonyl acetate was discharged but this could not be detected by IR or by UV and was doubtful with SLAR. It was apparent at this time that some chemicals were going to be easier to detect than others by airborne remote sensing (IR, UV and SLAR) and that it would be useful to conduct laboratory based experiments using a thermal imaging system on selected chemicals to obtain additional information and to determine which ones to use in sea trials.

3. EXPERIMENTAL WORK

The experimental work was carried out in the following stages:

(1) Selection of suitable chemicals.

(2) Qualitative small-scale testwork to see if thermal imaging can detect chemicals floating on water.

(3) Test tank trials to determine relative responses of the different chemicals to thermal imaging.

(4) Full scale trials using the MPCU aircraft with UV, IR and SLAR sensors to detect selected chemicals discharged at sea.

3.1 Selection of Chemicals

Chemicals used for the preliminary testwork and pilot-scale experimental work were selected to give variations of chemical and physical properties to use in seeking correlation with results of imagery.

Further considerations of safety, toxicity and availability were important criteria in deciding which chemicals to use.

The chemicals used in the testwork together with some physical properties are listed in Table 2.

TABLE 2. - Some Properties (at 293°K) of Chemicals Used in the Experimental Work

Chemical	Solubility in Water	Density	Vapour Pressure	Dielectric Constant	Surface Tension	Viscosity	Thermal Conductivity
	$Kg\,m^{-3}$	$Kg\,m^{-3}$	m bar		$N\,m^{-1}$ ($\times 10^{-3}$)	$N\,s\,m^{-2}$ ($\times 10^{-3}$)	$Wm^{-1}\,K^{-1}$
Amyl Acetate	2.5	880	6	4.75	24.7	NA	0.13
Benzene	0.7	880	100	2.28	28.9	0.65	0.14
Cyclohexane	insol	780	102	2.02	25.5	NA	NA
Cyclohexene	v sl sol	810	94	2.22	NA	NA	NA
Di Iso Octyl Phthalate	NA	990	1	NA	NA	NA	NA
Ethyl Acetate	85	900	100	6.02	23.9	NA	0.15
Hexane	insol	660	133-160	1.89	18.4	NA	0.15
Glycerol	∞	1260	<1	42.5	63	1500	0.27
Methanol	∞	790	127	32.6	22.6	0.59	0.20
4 Methyl Pentan-2-one	20	800	6	NA	NA	NA	NA
Nonyl Acetate	0.5	870	1	NA	NA	NA	NA
Octan-1-ol	0.5	830	1	10.3	27.5	NA	NA
Paraffin Liquid	NA	800	NA	NA	26	1000	0.15
Propan-2-ol	∞	790	19	18.3	23.8	NA	0.15
Styrene	v sl sol	910	6	2.43	NA	NA	NA
Toluene	insol	870	29	2.38	28.4	0.59	0.13
Xylene	insol	880	13	2.57	28.9	NA	0.11

NA denotes information not available

3.2 Preliminary Testwork

In a series of individual tests with 14 chemicals, each chemical was tested in turn by adding up to 50 cc of it to a sample of clean fresh water and examining the response through a Barr and Stroud IR18 thermal imaging scanner (Appendix A).

It was anticipated that the results would give an indication of what could be expected from the similar Rank Taylor Hobson equipment on the Cessna 404. Care was taken to equilibrate the chemical and water temperatures prior to recording the imagery.

The preliminary testwork demonstrated that thermal imagery could be used for detecting some chemicals on water. Ethyl acetate, benzene, cyclohexane, cyclohexene, hexane and toluene all gave definite but dark imagery compared with that for the background. This indicated that the floating chemical was emitting thermal IR radiation less efficiently than was the water at the same temperature.

Addition of methanol to water caused the imagery to appear lighter than before. The lighter imagery lasted less than ten seconds before returning to the previous grey level. This thermal effect was thought to be due to heat of solution. The propanol behaved similarly.

The styrene and amyl acetate both produced inconclusive results.

3.3 Pilot-Scale Experimental work

Fifteen chemicals were selected for the more rigorous pilot scale experiments.

The chemical under test was poured on to synthetic sea water forming an area of one square metre enclosed by a freely floating corral.

Different depths of the chemical, ranging from 1 to 5 mm, were formed as required and examined through a Rank Taylor Hobson thermal imaging scanner (Appendix A). The imagery was recorded on tape for later playback.

The equipment arrangement is shown in Figure 1 and hard copies of typical imagery obtained for two chemicals are shown in Figures 2 and 3.

The experimental work produced a range of thermal imaging responses with benzene, cyclohexane, 4-methyl pentan-2-one and toluene giving strong dark images. Diiso octyl phthalate, nonyl acetate and xylene gave definite but weak imagery.

Amyl acetate and octan-1-ol produced little or no thermal imagery.

3.4 Sea Trials

Sea trials were conducted on the following chemicals chosen after studying the results from the pilot plant experimental work.

Styrene
Cyclohexane
Toluene
Nonyl Acetate
Methanol
Paraffin

Styrene, Cyclohexane and Toluene were expected to give strong thermal imagery with easily detectable slicks. Nonyl Acetate was chosen as an example of a chemical that would be expected to produce weak thermal imagery. Methanol was included to provide a contrast to the other chemicals. It is soluble and forms a white turbidity in seawater. During the pilot plant trials, the turbidity lasted long enough to give a light image when viewed through the thermal imaging scanner. Paraffin liquid, although not tested during the laboratory based work, was included in the sea trials to provide additional information.

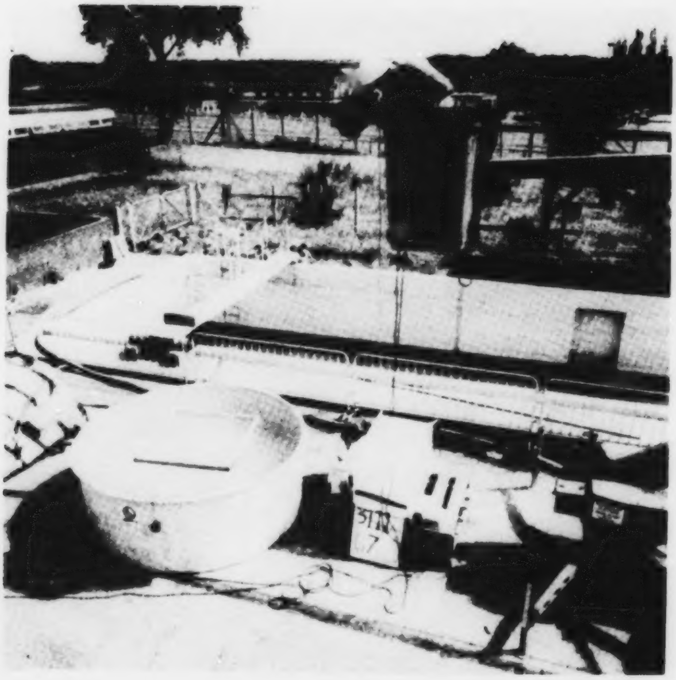


FIGURE 1. Pilot Scale Testwork using Rank Taylor Hobson Thermal Imaging Scanner

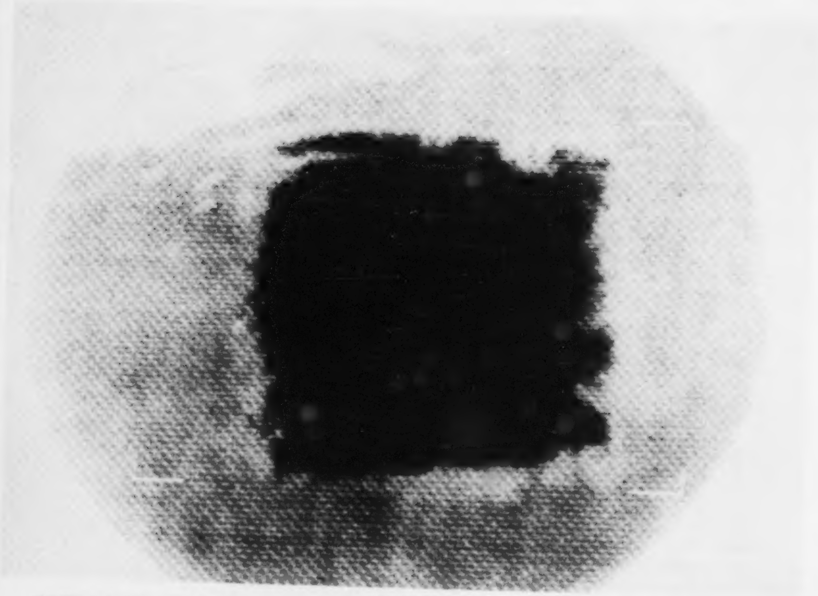


FIGURE 2. Pilot Scale Testwork - Imagery of Cyclohexane 2mm Thickness

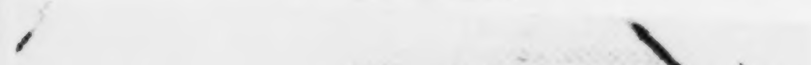


FIGURE 3. Pilot Scale Testwork - Imagery of Xylene 5mm Thickness

Although the temperature of the chemicals could initially be different from that of the sea, only a few seconds would be required for the temperatures to equalise to within 0.1°K following the discharge.

Table 3 gives the results of the airborne detection using the instruments on the Cessna 402 and 404 aircraft (Appendix A) together with the small scale and pilot scale results. Table 4 summarises the observations from RV Seaspring (the laboratory's research vessel).

TABLE 3. - Summary of Detection

Chemicals	Thermal Imaging Testwork		Sea Trials							
	Small Scale	Pilot Scale	Cessna 402				Cessna 404			
			IR	UV	SLAR	Visual	IR	UV	SLAR	Visual
Ethyl Acetate	3	3								
Glycerol	-	0								
Methanol	4	4	-	-	-	-	2	0	-	0
Propan-2-ol	4	4								
Amyl Acetate	1	1								
Benzene	3	3								
Cyclohexane	3	3	2	1	0	2	3	2	0	2
Cyclohexene	3	3								
Diesel Oil	4	4								
Diiso Octyl Phthalate	0	2								
Hexane	3	3								
4 Methyl Pentan-2-one	-	3								
Nonyl Acetate	0	2	2	0	-	2	2	2	-	2
Octan-l-ol	0	1								
Paraffin liquid	-	-	0	0	-	0	2	0	-	0
Styrene	1	-	-	-	-	-	3	4	-	4
Toluene	3	3	3	2	-	2	3	4	0	2
Xylene	0	2								

Key
0 denotes Not detected, 1 denotes Possible imagery, 2 denotes Definite but weak imagery, 3 denotes Strong dark imagery, 4 denotes White imagery, - denotes Not attempted

It was decided not the use the Cessna 402 in an attempt to detect the methanol discharge on account of the poor sensitivity of the detection equipment on board the aircraft.

SLAR monitoring of the discharge was limited by adverse weather conditions.

TABLE 4. - Sea Trial - Summary of Observations from Seaspring

Chemical	Discharge Rate ($1\ min^{-1}$)	Observations from Deck of Seaspring
Cyclohexane	90	Colourless slick, easily visible, up to 7 m wide
Toluene	50	Colourless trail of toluene with edges coloured due to refracted light. Up to 4 m wide.
Nonyl Acetate	100	Clear colourless slick up to 3 m wide.
Methanol	100	White turbidity which lasted 2-3 minutes before disappearing.
Paraffin liquid	110	Opaque, white, semi solid appearance - looked as though it would be very slow to disperse.

Examples of imagery from the remote sensing of the sea trials are shown in Figures 4, 5.

The results from the sea trials confirmed the expectations from the pilot scale experimental work. The chemical slicks were detected with varying success by airborne remote sensing. Of the four different detection systems (IR, UV, Video and SLAR) the best imagery from both aircraft was obtained using IR. In general, aircraft altitude had little effect on the quality of the imagery.

Slicks from the styrene, toluene and cyclohexane discharges were detected with strong dark IR imagery from heights of up to 1000 feet. However, it should be noted that continuous discharges of styrene during complementary 'chemical countermeasures' sea trials resulted in less intense IR imagery of the styrene slick. This may have been because of different weather conditions at the time of these trials.

The slick from nonyl acetate was also detected but the imagery obtained was weaker. It was still well defined in the IR but was very weak in the visible. The UV imagery for the nonyl acetate slick was inconclusive. Neither aircraft was able to detect the toluene and cyclohexane slicks using SLAR. Adverse weather conditions at the time of the sea trial curtailed the original programme and prevented the SLAR monitoring of other chemicals that had been due to take place.

The methanol was not expected to produce a well-defined slick like the other chemicals in the trial because of its high solubility but it was possible to detect the thermal effect in the sea at up to 40 metres from the discharge source.

Generally speaking, the detection systems in the C404 were more sensitive than the detection systems in the C402.

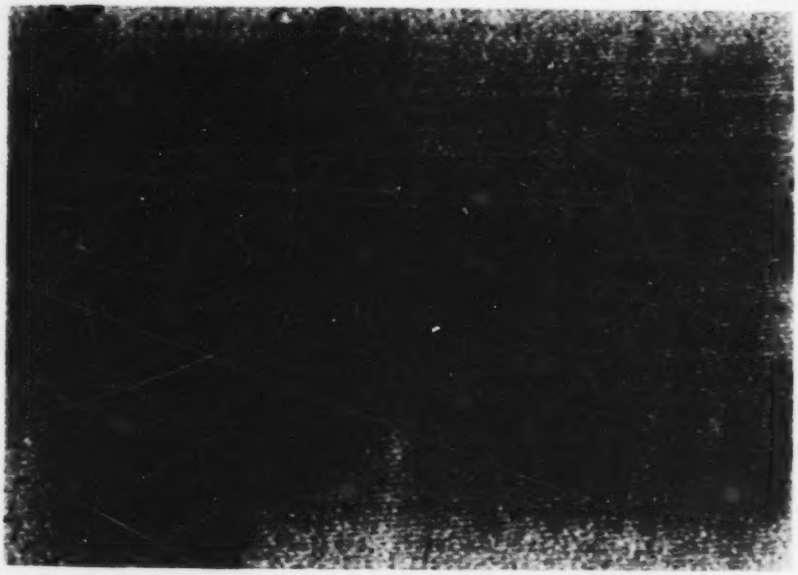


FIGURE 4. IR Imagery of Cyclohexane from Cessna 404 at 170 Feet

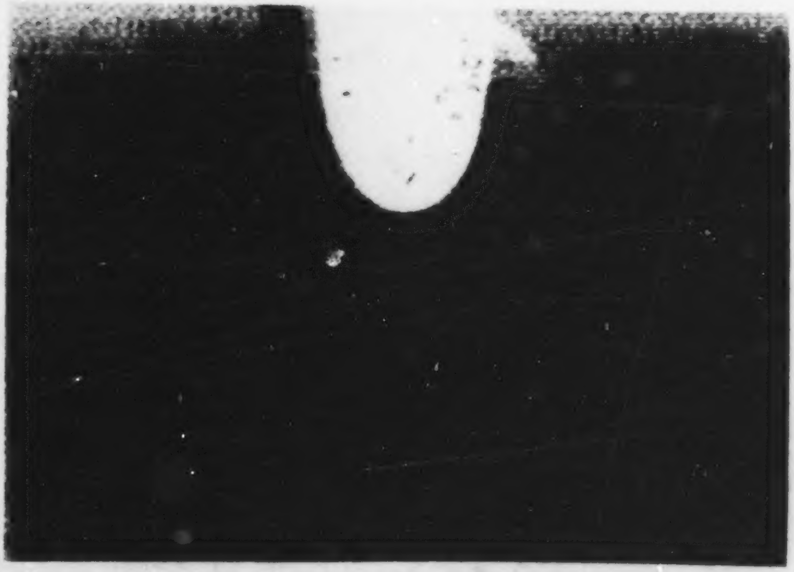


FIGURE 5. IR Imagery of Nonyl Acetate from Cessna 404 at 160 Feet

4. DISCUSSION

The mean slick thickness for chemicals discharged directly from "Seaspring" was estimated to be of the order of 600 micrometres. The styrene, having relatively low volatility, was discharged at the much lower rate of 2 litres/minute. In a 1 metre/second tidal current the mean depth of the slick was estimated to be of the order of 15 to 20 micrometres at a swath width of 2 metres. The airborne IR remote sensing of chemicals generally, and of styrene in particular, is a sensitive technique but it is unlikely that the strict conditions contained in regulation 5 of Annex 2 of Marpol 73/78 relating to the discharging of chemicals at sea could be enforced by the present system of IR, UV and SLAR monitoring in the two aircraft. The regulation is complex and covers such aspects as distance of the vessel from the nearest land, the speed of the vessel during the discharging and the category of chemical being discharged but a brief summary of some salient points in regulation 5 is as follows:

The discharging of category A chemicals at sea, even when such chemicals are in the form of dilute tank washings, is prohibited.

Category B and C chemicals can be discharged at sea but the discharge must be strictly controlled. The concentration of chemicals in the wake astern of the ship must not exceed 1 ppm for category B chemicals and 10 ppm for category C chemicals.

For category D chemicals the concentration in the discharge must not exceed one part of the substance in 10 parts of water.

The IR, UV and SLAR monitoring systems in the two aircraft cannot identify specific chemicals to determine to which category a chemical may belong and, although not investigated specifically, the sensitivity of the remote sensing instruments would almost certainly be less than required for the enforcement of regulation 5.

In the 8-14 micrometres region of the electromagnetic spectrum the emissivity of water is greater than 0.95 and water closely approximates that of a blackbody. Those chemicals having emissivity values appreciably below that for water are ones likely to be detected from the air using IR. The C404 equipment is capable of detecting real (and apparent) temperature differences, typically of less than 0.1°K. As the IR Line Scanning equipment in the C402 has a minimum detectable temperature difference of 0.5°K the C402 cannot be expected to perform as well as the C404. This was found to be the case during the sea trial.

Tables of emissivity values of engineering and building materials are common but unfortunately there seems to be a dearth of information on emissivities of liquid chemicals. Therefore it has not been possible to relate the ability to detect a given chemical to its emissivity. Similarly by reference to Tables 2 and 3 it can be seen that there is no clear correlation with other properties such as thermal conductivity, vapour pressure etc.

Results from the monitoring of chemicals using SLAR were variable. In practice, the ability of a spilled chemical to damp the capillary waves at the sea surface will depend on the physical properties of the chemical, the quantity spilled and the environmental conditions prevailing. It should not be assumed that SLAR can necessarily be used to locate a chemical slick in the same way as for oil.

5. CONCLUSIONS

Of the remote sensing techniques assessed here, the IR clearly gave the best imagery with slicks typically appearing in sharp contrast to the sea. Different IR systems have different sensitivities which affects the ability to detect chemicals. Nevertheless, in the event of a chemical spill incident it would probably be worthwhile sending an aircraft equipped with an IR system to investigate the situation and assess any pollution that may have occurred. UV imagery and visual observation might supplement detection by IR. Initial location of the slick using SLAR could be a problem - the results of the SLAR evaluation here were inconclusive.

It is not possible to identify specific chemicals using IR, UV, or SLAR instruments. Airborne Laser Fluorosensing (LF) systems have been under development for some years. A small area of sea under the aircraft is illuminated by a UV laser and the absorbed radiation is re-emitted at other wavelengths depending on the nature of the sea surface. The analysis of this response is very complex but, in principle, it could be used to identify specific chemicals.

From the work here, it does not appear possible at present to predict whether a given chemical could be detected by IR, UV or SLAR instruments unless that chemical has previously been evaluated in laboratory or sea trials. In any event, it is most unlikely that existing remote sensing aircraft could be used for the enforcement of Annex II of Marpol 73/78.

It may be possible to use IR systems to detect whether a soluble chemical with a high heat of solution is continuing to leak from a tanker.

6. ACKNOWLEDGEMENT

The work described here was funded by the Marine Pollution Control Unit of the Department of Transport of the UK Government.

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Appendix A

APPENDIX A: EQUIPMENT

The equipment that was used in the investigation is described as follows:

Small Scale Testwork

Barr and Stroud IR 18 thermal imaging scanner, operating in the thermal infra red (8-12 microns) region of the electromagnetic spectrum.

COHU 5802 (low light in the UV) camera.

Pilot Scale Testwork

Rank Taylor Hobson thermal imaging scanner, operating in the thermal infra red (8-12 microns) region of the electromagnetic spectrum.

Monitoring Equipment in C402

IR/UV

Frequency:	IR channel 8-14 microns; UV channel 0.3-0.4 microns
Resolution:	2 metres at 1000 feet
Field of View:	80 degrees
Minimum detectable temperature difference:	0.5°K (IR)

SLAR

Frequency:	X - band, 9.3 GHz
Polarisation:	Vertical
Peak Power:	10 kW
Resolution:	75 x 75 metres

Monitoring Equipment in C404

IR/UV

Frequency:	IR channel 8-12 microns; UV channel 0.3-0.4 microns
Resolution:	2.727 milliradian
Field of View:	60 x 40 degrees (625 line/50 Hz)
Minimum detectable temperature difference:	0.1°K (IR)

SLAR

Frequency:	X - band
Polarisation:	Vertical
Peak Power:	20 kW
Resolution:	75 x 75 metres

CONDUCTING HEADSPACE ANALYSIS USING DIFFERENT FIELD SCREENING TOOLS

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ABSTRACT

The U.S. EPA/ERT and REAC have used field screening instruments for the on-site analysis of Volatile Organic Compounds (VOCs) in various sample matrices. Headspace analysis, either in-situ, such as soil gas analysis, or via static/dynamic analysis of soils and waters, can yield information useful in determining the extent of contamination or to monitor removal and remediation activities.(1,2)

Various different types of field screening tools can be used in characterizing a site. These tools can be used alone or in concert to yield the greatest amount of site information possible within time and cost restraints. Three case studies will be used to illustrate the capabilities of the different field screening tools and their various applications for rapid on-site assessments.

The U.S. EPA/ERT has developed Standard Operating Procedures (SOPs) for field instrumentation and sampling protocols that can help assess and direct field activities in a real-time basis. The instruments listed in this paper are units for which the U.S. EPA/ERT has extensive field experience. The mention of specific manufacturers should not be considered an endorsement by the U.S. EPA/ERT in any way.

INTRODUCTION

Field screening instruments have been used for the rapid on-site assessment of environmental contamination at a variety of sites throughout the United States. The U.S. Environmental Protection Agency (U.S. EPA) has used field screening techniques to delineate the extent of contamination of both soils and groundwaters, to assess remediation activities, and to monitor fugitive emissions during site activities. Field screening techniques should be considered anytime the rapid generation of data on-site will result in better protection of the health and safety of the public, a reduction in the environmental impact on sensitive biota, and/or a savings in time and money by the proper use of limited site resources.

Headspace analysis by either in-situ soil gas analysis or via static/dynamic headspace analyses of soils and waters are limited to those compounds that are easily liberated from the soil or water matrix into the gas phase. Compounds with high bulk liquid vapor pressures and low solubility in water are best suited. The relationship of a compounds' vapor pressure and solubility is expressed in the Henry's Law Constant (Hc). In general, compounds with high Hc values respond well to field headspace techniques.(3) There are many site-specific mitigating factors that influence the use of headspace analysis. An in-depth analysis of all these factors is beyond the scope of this paper. The reader is directed to the bibliography for citations which explore the movement of vapor through soils, the thermodynamics of soil and water headspace equilibrium and other aspects influencing headspace analysis. A brief discussion of the major factors influencing field headspace analysis, as encountered by the U.S. EPA/ERT, will be presented.

In-situ headspace, or soil gas analysis, is dependent upon the diffusion of organic vapors through the air filled pores in the soil column. Many site-specific factors, such as soil porosity, moisture, organic content, temperature, grain size and surface area will affect the migration of vapors through the soil. As the moisture content of the soil increases, the nonpolar VOCs will preferentially desorb from the soil matrix into the water phase. Once in the water phase, the VOCs will volatilize into the gas phase under the influence of their Hc values to yield soil gases. If the soil moisture becomes too high, the air-filled pores in the soil matrix will be filled with water to the extent that soil gases will not be generated. Organic content in the soil will also have an effect on vapor migration, as many VOCs may solubilize into the organic layers of the soil and not be present as a gas. Ambient atmospheric conditions, such as atmospheric barometric pressure and ambient air relative humidity, will also affect the movement of soil gas through the soil column(4).

Headspace analysis of soils and water, by either static or dynamic techniques, are also influenced by site-specific sample matrices. This is especially true with soils where the rate limiting step is typically the movement of VOCs from the soil matrix into the water phase. Soil organic content, grain size and cationic content will dictate the rate at which the VOCs are liberated into the aqueous extractant solution (water phase).

Site specific matrix anomalies will vary from site to site. To address this, field calibration standards should be prepared using the same site-specific soils or waters as the samples. Therefore, any factors mitigating generation of headspace VOCs will be incorporated in the field calibration standards. Surrogates and internal standards can also be used to trace the recovery of VOC species from the soil or water matrices into the headspace phase.

METHODS AND MATERIALS

In-situ headspace screening, or soil gas analysis, can be used to determine the presence and extent of subsurface contamination either in the soil column or underlying ground waters. Soil gas samples are collected using bore hole techniques such as a manual slam bar probe. Soil gas samples are stored in inert teflon sample bags or other appropriate vessels prior to analysis. The samples are first analyzed using non-analyte specific screening tools, such as the Century OVA Model 128 (Foxboro, MA, USA) and the HNu Model PI101 (NHu System, Inc., MA, USA), to yield an indication of the level of contamination. The same soil gas samples are then submitted for on-site analysis using commercially available field portable gas chromatographs (FPGCs). FPGCs will yield information of both the identity of the VOCs species and its corresponding concentration.(5)

Soils and waters can be analyzed for the presence of VOCs by either static or dynamic headspace techniques. Static headspace is the easier of the two soil/water screening techniques. A 20 milliliter (ml) aliquot of aqueous samples is placed into a clean 40 ml vial, with a teflon lined screw cap. The vial is securely sealed, shaken vigorously for one minute and inverted to affect a water seal. The samples will equilibrate with the VOCs partitioning between the bulk liquid and vapor headspace phases as per their Hc values. After 30-60 minutes equilibration time, the vial is righted and the space above the bulk liquid phase, the headspace, is sampled for FPGC analysis of VOCs. For soils, 1-10 grams of the sample are placed in the 40 ml vial. Approximately 10 ml of distilled deionizing water is added, such that the total volume in the vial is 20 ml (soil plus water). The vial is capped securely, shaken vigorously for one minute, and left quiescent for 30-60 minutes. The vial is not inverted. The headspace is sampled for subsequent FPGC analysis of VOCs.

Static headspace samples are simple to prepare, requiring no special or optional pieces of equipment. It is assumed that the 30-60 minutes is a sufficient period of time for an equilibrium to be established between the soil-water slurry and headspace phase. Certain site specific sample matrices, especially certain soils, may require longer periods of time to equilibrate. It is important that the volume of sample, headspace volume and equilibration time be held constant for all samples and standards in order for the calibration to be valid.(5)

Dynamic headspace techniques employ a field portable purge and trap sample concentrator. A simple dual adsorption trap unit was developed by Louisiana State University (LSU) for the U.S. EPA/ERT. Water samples and soils in a soil-water slurry are purged for two minutes with helium to scrub the VOCs out of the water or soil matrix and onto one of the adsorption traps.

The traps are packed with Tenax/Spherocarb and are at room temperature during collection of the purged VOCs. The trap is then rapidly heated to 240°C, held at that temperature for one minute, and then backflushed with helium to thermally desorb the VOCs off the trap and into a gas-tight syringe. The syringe is then submitted to the FPGC for VOC analysis. The second trap allows a second sample to be purged while the first trap returns to room temperature, thereby increasing sample through-put.(6)

Dynamic headspace techniques are typically faster and more complete than static headspace methods. Most purgeable VOCs will be scrubbed from the soil and water within the first few seconds. Procedures must be taken to document that the traps are working correctly. A surrogate or internal standard can be spiked into each sample to assess trap performance.(7)

The sample concentration is manually operated and is of simple design. It can be fabricated from commercially available parts at a cost under $2,000 - $3,000. It operates under 110 VAC power, although LSU has also built 12 volts DC battery-operated units.

Several different commercially available field instruments are currently used by the U.S. EPA/ERT. Three case studies will be cited to highlight the different instruments and the applications for which they are suited.

CASE STUDY #1

In March 1989, a bank exploded in an old mining region in Colorado, resulting in several fatalities and extensive damage to property. The bank was adjacent to an old marsh and was in close proximity to an underground propane gas line. Three different scenarios were suggested as to what was the source of the explosive gases.

The obvious consideration was a possible ruptured propane gas line which allowed propane to migrate through the soil and to reach explosive levels in the basement of the bank. Another theory was that methane gas was being generated in the adjacent marsh and that it accumulated in the basement of the bank. The final theory was that methane from abandoned mine shafts, of which many were present in the area, could possibly have migrated through the geological strata and fissures and up through the soil column where it collected in the basement of the bank.

Soil gas samples (in-situ headspace) were collected using a manual slam bar soil probe around the bank, the marsh and along the underground propane gas line. A soil vapor extraction (SVE) system was installed to pull the residual methane and/or propane out of the soil. Soil gas sampling was used to monitor the effectiveness of the SVE system, as well as to track the source of explosive gases. Basements and crawl spaces of nearby houses were screened for explosive gases using both the OVA 128 and an explosivity meter.

The OVA 128 cannot distinguish between methane and propane, both yield positive responses. A chromatographic separation column was needed to separate the highly volatile methane and propane species. The OVA 128 was converted from the screening mode to the gas chromatography mode (OVA128 GC). A simple syringe injection port was attached to the unit, along with a 14 foot by one-eighth of an inch outer-diameter Teflon tube OV101 column (14' x 1/8" O.D., OV101). Soil gas samples were screened by the OVA 128 and then submitted to the OVA 128 GC to determine methane and propane. Summa canisters of soil gas samples were taken for gas chromatography/mass spectrometry (GC/MS) confirmatory analysis. The GC/MS data verified the on-site analysis of the OVA 128GC FPGC. The OVA 128 GC was able to rapidly determine that propane and methane were the source of the explosive gases.

CASE STUDY #2

In October 1990, a train derailed in Tennessee releasing chloroform and styrene onto adjacent soils and drainage ditches. Local hydrogeological conditions (KARST) allowed the chemicals to rapidly pass through the soil column into the groundwater aquifer. Numerous underground streams and sink holes dispersed the contaminants into nearby wells and surface waters. Fast on-site analysis of soils and waters was required to delineate the rapidly spreading plume and to direct where remediation activities should be concentrated.

A Microsensor model P200 FPGC (Fremont, CA, USA) was used with the portable dual trap sample concentrator to perform dynamic headspace screening of soils and waters. The P200 FPGC was able to analyze samples for both chloroform, styrene and several other VOCs in under ten minutes per sample. Detection limits were in the 20-50 parts-per-billion (ppb) range.

The P200 FPGC uses dual capillary columns and dual micro-chip thermal conductivity detectors (μTCD's). The dual analytical system increases the level of confidence in the peak identification routines since one column acts as the confirmation column of the second. In addition, the P200 software allows an identification library of 100 VOCs to be updated using a field calibration standard of only three or more VOCs. As a result, many VOCs present in the library, but not present in the field calibration standard, could be tentatively identified if present in the sample. This is extremely useful when the exact nature of the contaminant species is not well known.

The ability to yield tentatively identified VOCs was found to be very useful at this site. An unexpected compound, Trichloroethane (TCE), was detected in the water samples. Since TCE was not one of the chemicals released during the train derailment, it was not present in the field calibration standard. The identification library routines were able to tentatively identify the TCE based on library values only. Further confirmatory analysis verified that TCE was indeed present in the samples. There was apparently a previously unknown plume of TCE contamination that was unrelated to the train derailment.(8)

CASE STUDY #3

The contents of approximately 150 drums of organic and metal wastes were illegally dumped on a six-acre wood lot in southern New Jersey. An estimated 1200 cubic yards of contaminated sludge and solids were present. Extensive soil contamination resulted. The U.S. EPA mandated that the soils be removed for off-site treatment. The U.S. EPA/ERT was tasked to define the extent of soil contamination. ERT identified the lateral and vertical zones requiring excavation.

A shallow soil gas (in-situ headspace) survey was initiated to delineate the extent of subsurface soil contamination both laterally and vertically. The soil gas samples were first screened via the HNu PI101 to determine overall contamination. The same soil gas samples were then submitted to on-site Photovac 10S50 FPGCs to identify and quantify the VOCs present.

From the soil gas survey, areas of high contamination were isolated. From these regions, soil samples were taken both across the area laterally and at several depths (vertically). The samples were screened using the static headspace technique to determine the VOCs present in the soils. Several visits were required to pinpoint the areas of both off and on-site contamination in an attempt to remove only those soils requiring off-site treatment.

Initial soil gas results did not correlate well with the static headspace soil results. The soil gas survey had high levels of VOCs, while the collocated soil samples yielded low levels of VOCs. Groundwater samples were fairly clean indicating that no soil gas was being generated from the underlying aquifer. The coarse sand matrix and low VOCs soil results suggested that VOCs may have been lost during soil sampling and handling prior to standard static headspace analysis. As a result, the static headspace methodology was modified to reduce VOCs losses.

Soil samples were placed in pre-weighted sample vials to approximately half the volume of the vessel. The vessel, with Teflon lined screw cap, was immediately sealed. The sample was reweighed to determine the amount of the soil collected. The soil samples in the vials were equilibrated for 30-60 minutes, and the headspace was sampled. No water was added through the screw cap. The modified static headspace analysis yielded data more consistent with the soil gas survey data.

On the final site visit, over 150 soil samples were screened by the Photovac 10S50 FPGC via static headspace. A Viking model SpectraTrak 600 field portable GC/MS system was brought on-site to confirm the qualitative identification of the Photovac FPGC data.

A description of the site contamination, both horizontal and at depth, was developed using the in-situ headspace soil gas data and the static headspace soil data. As a result, 960 cubic yards were removed from the site for off-site remediation.

CONCLUSIONS

Various field screening tools can be used either by themselves or in concert with other field screening instruments to generate rapid on-site data. This data can be used to delineate the extent of contamination, direct remediation efforts and to assess site removal activities. Headspace analytical techniques can be used to screen to VOCs in air, water or soil matrices. Compounds with high Hc values respond best to headspace techniques. Many site-specific conditions can influence the effectiveness of headspace screening efforts.

The U.S. EPA/ERT has developed SOPs for on-site sampling, analysis and quality assurance and control criteria. On-site screening can result in savings of time and materials when conducting extent of contamination studies and removal or remediation activities.

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DEVELOPMENT OF A MOBILE GC/MS/MS SYSTEM FOR EMERGENCY RESPONSE

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INTRODUCTION

During chemical fires and spills, on-site air monitoring results can assist the site commander in evaluating the air quality, thus determining the appropriate course of action. Initially, the Emergency Response Team of the Air Resources Branch relied solely on the Trace Atmospheric Gas Analyzer (TAGA) for emergency air monitoring, which is based on Atmospheric Pressure Chemical Ionization (APCI) MS/MS. This has proven to be invaluable for tracking contaminants, especially polar compounds, in real time and at trace levels. However, APCI lacks sensitivity for detection of certain volatile organic compounds (VOCs) such as aromatic and chlorinated hydrocarbons. This led to the development of a new MS/MS system, utilizing a gas chromatograph (GC) interfaced with a low pressure Chemical Ionization (CI) source. VOCs, concentrated on a solid adsorbent, are thermally desorbed into the GC, containing a high resolution fused-silica capillary column. The GC effluent then enters the CI source where specific VOCs are ionized prior to MS/MS analysis. The system employs Macintosh based custom data acquisition and analysis software. This paper will briefly describe this mobile GC/MS/MS technique and some preliminary results.

THE MOBILE

The host vehicle for the TAGA 6000 is a ten metre Orion coach specially designed as a completely self-contained mobile laboratory for air monitoring. The layout of the mobile laboratory is illustrated in Figure 1. Equipment included in the mobile are two computer work stations, 17.5 kw generator, meteorological station with retractable tower, fume hood, refrigerator, and communication package. The computer work stations allow direct control of the instrument. The automatic start feature permits unattended generator power-up of the instrument prior to the monitoring day. A stable temperature is maintained inside the mobile by roof mounted air conditioners or wall mounted electric heaters. Its valuable contents are protected by a halon fire extinguishing system. The meteorological station monitors atmospheric temperature, humidity, wind speed, and wind direction at a tower height of ten metres. The fume hood and the fridge are used to store chemical standards. The communication package includes: a cellular phone for outside contact, a fax machine for data and information transfer, and a two-way radio for local communication among survey members in different vehicles.

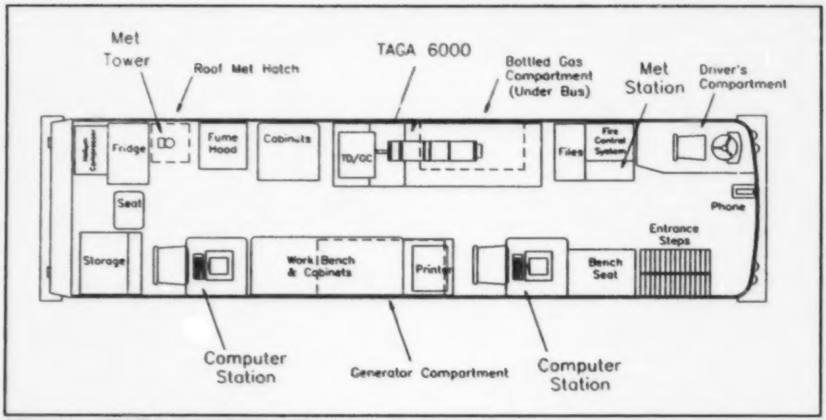
Met Tower
Roof Met Hatch
TAGA 6000
Bottled Gas Compartment (Under Bus)
Met Station
Driver's Compartment
Fridge
Fume Hood
Cabinets
TD/GC
Files
Fire Control System
Seat
Phone
Entrance Steps
Storage
Work Bench & Cabinets
Printer
Bench Seat
Computer Station
Generator Compartment
Computer Station

Figure 1: TAGA 6000 Mobile Laboratory Floor Plan.

INSTRUMENTATION

The TAGA 6000 MS/MS analyzer

The TAGA 6000 front end can be operated under one of the two ionization modes: APCI mode or CI mode. During the past decade, all the TAGA monitoring surveys were conducted using APCI. The ambient air is drawn directly into the APCI front end, operating at atmospheric pressure, at 100 L/min from the roof top inlet. Ionization of pollutants is accomplished through a series of gas-kinetic, chemical

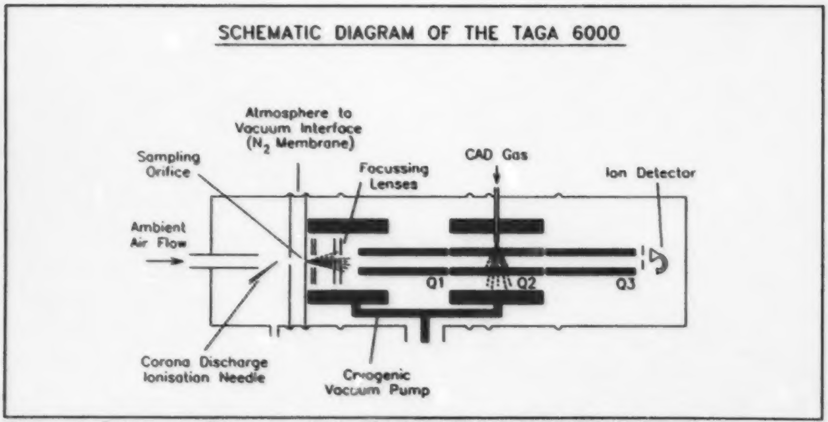
SCHEMATIC DIAGRAM OF THE TAGA 6000
Atmosphere to Vacuum Interface (N_2 Membrane)
Sampling Orifice
Focussing Lenses
CAD Gas
Ion Detector
Ambient Air Flow
Q1
Q2
Q3
Corona Discharge Ionisation Needle
Cryogenic Vacuum Pump

Figure 2: Schematic Diagram of the TAGA 6000 APCI/MS/MS System.

ionization reactions, initiated by a corona discharge. After penetrating a nitrogen curtain gas, which prevents minute particulate matter from blocking the 100 micron sampling orifice, ionized pollutants are subjected to MS/MS analysis. A schematic diagram of the TAGA APCI/MS/MS system is shown in Figure 2. Detailed description of the TAGA instrument operated under the APCI mode was previously presented[1]. It has been shown that the APCI is extraordinarily sensitive to polar compounds. However, APCI is not sensitive for detection of certain volatile VOCs such as aromatic and chlorinated hydrocarbons at ppb levels. Sensitivity to these compounds is improved by changing the front-end interface to CI mode.

The CI mode is a low volume (5-10 mL/min), heated glow discharge chemical ionization operating in the pressure range of 0.1 to 10 torr. A schematic diagram of the TAGA CI/MS/MS system is shown in Figure 3. Electrons emitted from the townsend discharge electrode are energized by a discharge counter electrode into the source block/orifice plate region. These electrons first react with molecules of the bulk gas to form positive and/or negative reagent ions such as NO^+ and O_2^-, which subsequently react with the trace samples to from trace ions. Trace ions are sampled through a 1 mm orifice under the influence of gas flow into the TAGA vacuum chamber and are subjected to MS/MS analysis.

Trace samples may be introduced into the CI source by one of the three ways: as an effluent from a GC, by desorption from the Direct Insertion Probe (DIP) or as a direct air sample via the Direct Air Sampling Inlet (DASI). For this analytical application, GC is the preferred choice.

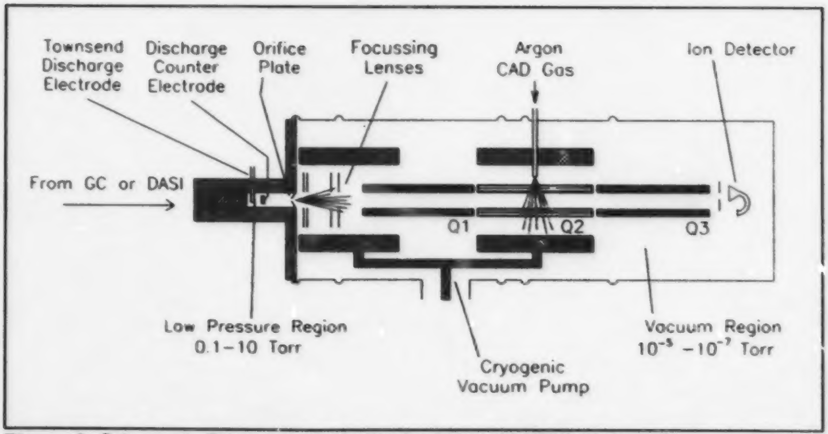
Townsend Discharge Electrode
Discharge Counter Electrode
Orifice Plate
Focussing Lenses
Argon CAD Gas
Ion Detector
From GC or DASI
Q1
Q2
Q3
Low Pressure Region 0.1–10 Torr
Cryogenic Vacuum Pump
Vacuum Region 10^{-5} – 10^{-7} Torr

Figure 3: Schematic Diagram of the TAGA 6000 CI/MS/MS System.

Gas Chromatograph

A Varian 3400 GC equipped with a capillary column is interfaced to the CI source by a customized GC transfer line. Sample components are separated by the capillary column according to their retention times, which depend on their affinity for the stationary liquid phase and the mobile gas phase.

Thermal Desorber

The air sample collected on an adsorbent cartridge is introduced to the head of the GC column by an Envirochem model 810 thermal desorber (TD). The TD employs an external desorber to transfer the air sample to two internal traps which are used for focusing the sample prior to delivery to the GC separation followed by CI/MS/MS analysis.

EXPERIMENTAL

The main objective was to expand the TAGA's capability to monitor VOCs. Table 1 lists 16 selected VOCs which have been thoroughly studied.

Table 1

Hydrocarbons	Chlorinated Hydrocarbons
Isoprene	Vinyl chloride
Hexane	Tetrachloroethylene
Benzene	Chlorobenzene
Toluene	1,1,1-Trichloroethane
Ethylbenzene	1,1,2-Trichloroethane
o-Xylene	Dichloromethane
1,3,5-Trimethylbenzene	1,2-Dichlorobenzene
Butylbenzene	Bromodichloromethane

For quantitative analysis, it was necessary to develop a dilution system to generate gas standards prior to the TD/CI/MS/MS study. Two certified gas cylinders, one containing a mixture of the 8 selected hydrocarbons and the other containing a mixture of the 8 selected chlorinated hydrocarbons, supplied by Matheson Gas Products Co. (Whitby, Ontario), had a nominal concentration of 20 ppm for each compound. Desired concentrations are obtained by altering the zero air dilution, and the mass flow controlled rates from the certified cylinders. Zero air is produced in-house by an AADCO 730 pure air generator.

Other experiments performed during this development were: GC temperature program modification, GC linearity study, Gilian portable air sampler evaluation, capillary columns comparison, and desorption efficiency and memory effect determination of the solid adsorbent media.

RESULTS AND DISCUSSION

Initially the TD/GC/CI/MS/MS study was conducted using a Varian 3400 GC equipping with a J&W DB-5 capillary column (15m x 0.25mm ID x 0.25μm film thickness). However, the DB-5 capillary column lacked resolution for adequate separation of VOCs, particularly vinyl chloride, isoprene, dichloromethane and hexane. A sample chromatogram of the 16 compounds analyzed by the DB-5 capillary column is shown in Figure 4.

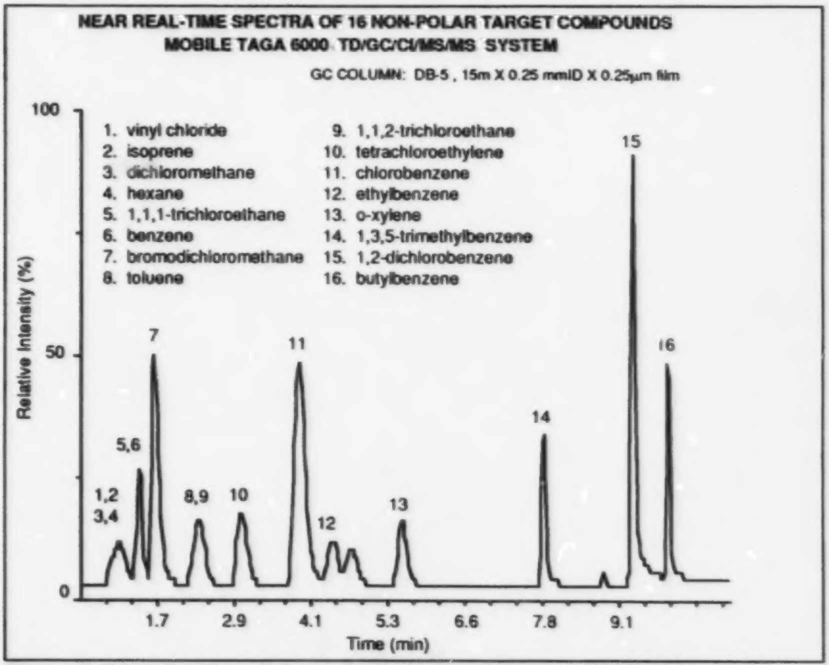

Figure 4: DB-5 Capillary Column Analysis of 16 VOCs via TD/GC/CI/MS/MS.

Published studies using a J&W DB-624 megabore capillary column (30m x 0.53mm ID x 3μm film thickness) indicated that it would resolve most of the target compounds with molecular weights ranging from 60 to 164 amu, within 30 minutes and without the need of cryogenics[2]. Figure 5 is a typical chromatogram of the 16 compounds analyzed by the TD/GC/CI/MS/MS system using the DB-624 megabore capillary column. Most of the compounds are well separated by the column. Note that isomers 1,1,1-trichloroethane and 1,1,2-trichloroethane are separated by more than 2 minutes. However, 1,2-dichlorobenzene and butylbenzene coelute at retention time of about 9.9 minutes; using the MS/MS capability of the TAGA, the two compounds are easily distinguished.

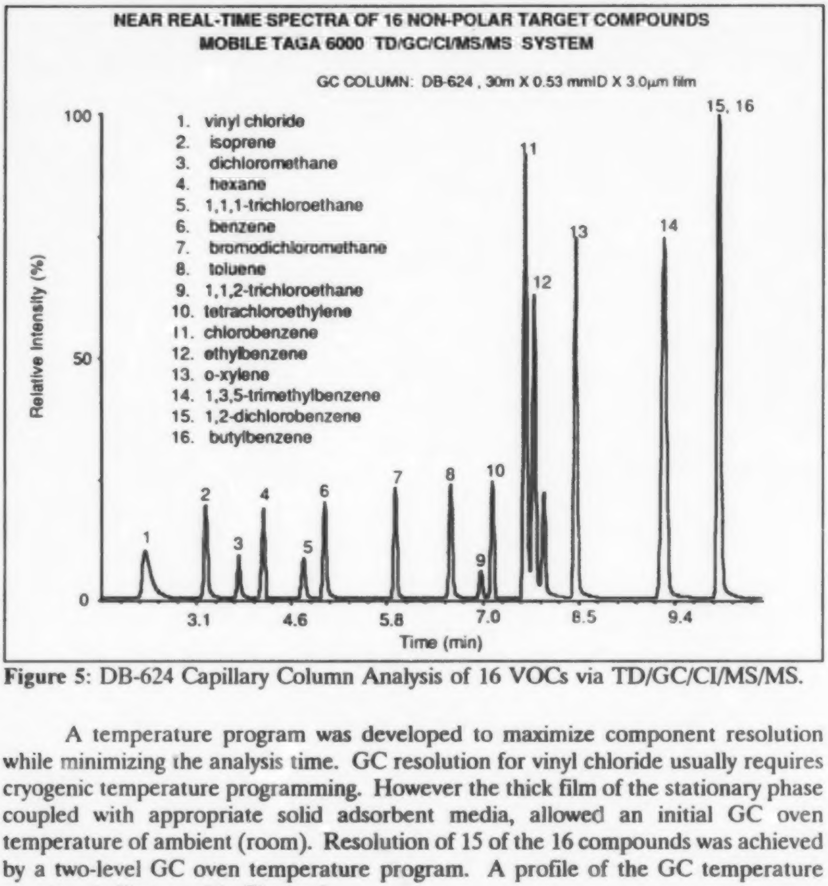

Figure 5: DB-624 Capillary Column Analysis of 16 VOCs via TD/GC/CI/MS/MS.

A temperature program was developed to maximize component resolution while minimizing the analysis time. GC resolution for vinyl chloride usually requires cryogenic temperature programming. However the thick film of the stationary phase coupled with appropriate solid adsorbent media, allowed an initial GC oven temperature of ambient (room). Resolution of 15 of the 16 compounds was achieved by a two-level GC oven temperature program. A profile of the GC temperature program is illustrated in Figure 6.

Studies were also conducted to determine the desorption efficiency and breakthrough volumes of various solid adsorbents. Although different solid adsorbent media had been tested, the current version of the sampling cartridge consists of glass beads, Carbotrap B, Carbotrap C, and Carbosieve S-III. This cartridge arrangement was used to obtain the data shown in Figure 5. Silanized glass beads are used to trap compounds of high molecular weights. Carbotrap B and Carbotrap C graphitized carbon blacks are ideal adsorbents for trapping a wide range of airborne organic compounds, mainly C_5-C_8 compounds and other large molecules. The Carbosieve S-

III spherical carbon molecular sieve is excellent for trapping C_2 hydrocarbons and other small airborne molecules.

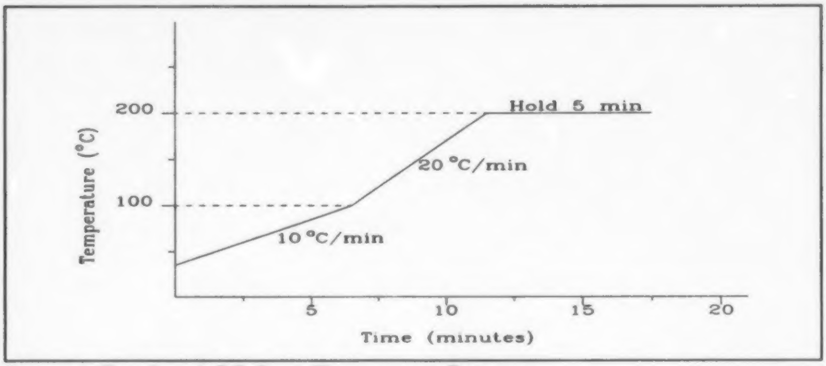

Figure 6: Two-Level GC Oven Temperature Program.

CONCLUSIONS

The mobile GC/MS/MS system was completed in April 1992. Cartridge field samples can now be analyzed on-site immediately after sampling. Sampling and analysis are performed in about one hour. In cases when concentrations of air contaminants exceed Ministry criteria, additional samples can be collected at the same site and under the same condition, in order to confirm the findings and more importantly, to locate the exact source of emissions. Another advantage of the mobile system is its ability to operate under either mode: APCI mode for polar compounds and CI mode for non-polar compounds. The time required to switch between APCI and CI modes is approximately 4 hours. Concurrently with monitoring using APCI, cartridge field samples can now be collected for subsequent CI analysis at a later time. Addition of the GC/MS/MS system expands the mobile system's ability to monitor a wide range of air contaminants. During emergency response, on-site air monitoring data can be acquired in minimum time, thus assisting the site commander in evaluating the air quality to help determining the appropriate course of action.

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THE USE OF A REMOTELY OPERATED UNDERWATER VEHICLE (ROV) DURING CHEMICAL SPILLS AND UNDERWATER INVESTIGATIONS. David W. Charters [1], Rodney D. Turpin [1], and William Van Derveer [2]. [1] U.S. EPA/Environmental Response Team (MS-101), 2890 Woodbridge Ave., Edison, New Jersey 08837-3679 [2] Roy F. Weston, Inc./REAC, 2890 Woodbridge Ave., Edison, New Jersey 08837-3679.

INTRODUCTION

The United States Environmental Protection Agency's (U.S. EPA) Environmental Response Team (ERT) is located in the Office of Solid Waste and Emergency Response. It was established in October 1978 to provide technical assistance to other branches of the U.S. EPA, as well as other Federal, state, and foreign government agencies in the area of environmental emergencies, such as chemical releases and uncontrolled hazardous waste sites. The ERT supports hazardous waste site cleanups under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) as amended by the Superfund Amendment and Reauthorization Act (SARA) and is supported in this role by the Response Engineering and Analytical Contract (REAC).

Hazardous waste dumping is not restricted to terrestrial environments. Two-thirds of the earth is covered by water, and this resource has been used both legally, illegally, and accidentally for the disposal of hazardous waste. Health and safety protocols are extensive for the proper protection of workers at terrestrial sites, but the protection of personnel working underwater has not been as extensively studied. There are multiple Level A suits for proper protection from a variety of chemicals in a non-aquatic situation, but there are few suits for the protection of divers and none of these suits were devised for protection of divers from hazardous chemicals. Breathing apparatus can be exposed to corrosive environments and fail. Many chemicals penetrate rubber and the high pressure hoses, resulting in unanticipated dermal contact or breathing chemicals under high pressure. The response community and the divers utilized have, in the past, not fully anticipated exposure of divers. In one simulation conducted by EPA, volunteer firemen who were assisting would have been killed or severely injured because of the erroneous assumption that dry suits are really completely dry.

Searches conducted by divers can be very time consuming, expensive, and hazardous. Searches for hazardous drums, tanks, radioactive waste containers, and other dangerous waste underwater usually can not be done from a distance due to restricted visibility. An unexpected "discovery" of a radioactive drum or even one's presence in close proximity can result in injury or, in a worst case scenario, death.

Safety considerations for divers must be fully evaluated before divers are allowed to enter the water. There are generally two steps that should be undertaken to evaluate the environment that the divers will have to enter. First, chemicals should be identified and concentrations evaluated. Second, there should be a visual reconnaissance to identify potential hazards such as piled drums and overhangs. If potentially hazardous items are discovered, are they labeled, intact, violated, empty, rusted ? The ERT has successfully utilized a remotely operated underwater vehicle (ROV) to conduct searches and evaluate underwater hazardous wastes. These searches and evaluations have ranged from confirming containers of arsenic trioxide lost off a container ship to a 55-gallon drum search and inventory in a limestone quarry to the discovery of sunken swimming rafts.

In potentially hazardous situations, an ROV can be utilized to replace divers for any direct observation task and is superior for search and observe tasks. As stated earlier, a benefit of utilizing an ROV is that it eliminates the possibility of diver exposure to hazardous substances and conditions. There is also the potential for longer-term operations; unlike divers, an ROV can operate without consideration of decompression tables which restrict the time a diver can be safely submerged. An ROV can be fitted with remote sensing devices such as sonar, that extend search capabilities into areas where direct observation is limited or impossible due to limited visibility. Finally, there are significant cost savings generated by ROV usage as opposed to divers. These savings are a result of restricting the need for commercial divers and providing associated support and equipment, such as personal protective equipment (PPE), air cylinders, and compressors. A drawback to ROV operation is that, although it can be outfitted with an articulated arm, it cannot perform activities requiring human dexterity.

VEHICLE SPECIFICATIONS

The base configuration of an ROV system consists of the vehicle, an umbilical cable, a command console, a monitor, and peripheral equipment, such as sonar and tracking systems. The system utilized by the ERT is a Benthos, Inc. MiniROVER MKII self-propelled system equipped with low light, high-resolution color graphics, color imaging sonar (Simrad Mesotech Limited, Mesotech 971), and ultra-short baseline (USB) acoustical tracking systems (ORE, Inc. Trackpoint II).

The submersible is an open-frame unit equipped with high torque horizontal, vertical, and lateral thrusters, pan and tilt video camera, two 150 watt underwater lights, a flux gate magnetic sensor (compass), and a pressure (depth) sensor. Affixed to the submersible frame are a sector/side scanning sonar head and acoustical tracking system transponder. The submersible is connected to the surface, via a 500-foot multi-conductor umbilical cable, to a control console.

The control console interface includes the ROV controllers and the transformers which convert AC current to the DC current utilized by the vehicle. The submersible is operated by a hand controller, resembling the type utilized by model aircraft enthusiasts, and allows movement in three dimensions. Underwater video images are sent through the umbilical to a monitor and video recorder for synchronous viewing and documentation. These images include an 86° horizontal by 55° vertical view of the area in front of the submersible, depth, compass bearing, number of umbilical turns, and date/time.

Sonar data are relayed through the console to a SIMRAD Mesotech, Inc. Model 971 sonar processor. The sonar system operates by transmitting a pulsed, short-duration, high frequency acoustical beam through the water column. Acoustical energy is reflected back to the sonar head by objects with acoustical properties different from their surroundings (targets). Based on the delay time, target distance and shape is determined by the sonar processor which, in turn, generates a high resolution color video image. The image is received by a monitor/recorder system, also with synchronous viewing and recording capabilities.

The O.R.E., Inc. USB tracking system operates independently of the other systems, utilizing the water column as the medium for signal transmission. The components of this system include a dedicated control console with color monitor, a transmitter/receiver (hydrophone), and the transponder attached to the submersible. A signal of consistent rate, intensity, and duration is generated by the console and transmitted by the hydrophone. This signal is received by the transponder and a response signal is then sent by the transponder and received by the hydrophone. Based on the returning signal direction and elapsed response time, the console calculates the position (bearing, horizontal range, and linear distance) of the submersible relative to the hydrophone or another fixed point as programmed. This information combined with the depth reading from the vehicle one can calculate the exact location of the vehicle in space. Both the sonar and tracking systems can be interfaced with a computer via an RS-232 connector to allow objective-specific programming and data logging.

CASE STUDIES

Arsenic Trioxide Search

Four cargo containers of arsenic trioxide were among twenty-one containers lost from the deck of a cargo vessel during a storm encounter offshore of the mid-atlantic coast. These containers were loaded with a total of 441 steel drums of powder arsenic trioxide, and were thought to have been lost during a period of peak storm intensity. Winds gusting up to 70 miles per hour (mph) were encountered approximately 30 nautical miles offshore of southern New Jersey. The threat to marine biota and subsequent human health risk in this commercial fishery zone prompted an emergency search for the lost arsenic containers. The United States Coast Guard coordinated the search and provided the On-Scene Coordinator for the search and recovery operations. The initial stages of the search, once the loss of the containers was discovered, was conducted by the U.S. Navy utilizing magnetic anomoly detectors deployed from helicopters. The helicopters localized areas which showed magnetic anomalies which could potentially be caused by metal shipping containers.

Once the anomalies were located the EPA's Ocean Survey Vessel, PETER W. ANDERSON, was utilized to further delineate the magnetic anomalies utilizing the vessel's side scan SONAR. A SONAR pattern indicative of shipping containers was rapidly discovered in approximately 30 nautical miles off Atlantic City, New Jersey, in about 130 feet of water. While the shape of the targets gave a good indication that the field was the area of interest, only four of the 24 containers held any real interest. The difficulty in identifying each container presented a significant problem with the anticipation of storms in January and early February in the Atlantic Ocean off New Jersey. The ERT was requested to provide visual identification and videotape the targets located with the sonar equipment.

The depth at which the ROV was used created a special problem in the time required to "fly" the vehicle to the bottom when working in relatively short weather windows. A sled was fabricated as a device for deploying the submersible in this deep water/high surface current environment. The submersible was rapidly lowered to the ocean floor utilizing the ship's winch and automatically released upon impact with the bottom substrate. The sled allowed us to save valuable minutes deploying the ROV and also allowed the ROV to be placed more precisely on the bottom.

The submersible was deployed in the vicinity of the benthic anomalies and operated more or less continuously for 11 hours, using the ROV sonar system for target location and submersible navigation. Down time was accounted for when it became necessary for the vessel to be moved. The expertise of the ANDERSON's crew and master were a critical factor in the success of this operation. Three cargo containers were found and evaluated. The containers and their cargo were identified by referencing external placards and identification numbers with the cargo vessel's manifest. One of these was a severely damaged and empty container originally containing the arsenic trioxide. The other containers held non-hazardous cargo also lost from the same vessel. At this point, the weather turned and we were driven back into port and the search was turned over to a recovery vessel also equipped with an ROV. This information confirmed that the field being evaluated was, in fact, the area of concern. The drums are now being recovered from the debris field.

Use of the ROV permitted a time and cost effective positive identification of the containers and narrowed the focus of the search to a localized area. This facilitated the initiation of an intensive search by other agencies and, ultimately, the location and recovery of the lost arsenic trioxide cargo.

Limestone Quarry

This site consisted of a bankrupt steel production facility and an unnamed limestone quarry in an urban area of the eastern central plains. A drum impoundment area situated immediately adjacent to the quarry and several visible drums in shallow water prompted suspicions as to the disposal of drums into the quarry. Preliminary sampling revealed highly basic (pH of nearly 13.0 units) surface water conditions. Due to the high pH and suspicion of unknown contaminants, the ROV was utilized to locate, characterize, and inventory submerged drums on the quarry floor.

The ROV search was initiated to determine the number of drums in the water and around the drum impoundment and determine if the drums were intact. The search was conducted to determine how these drums might be recovered. The ROV survey and concurrent water sampling revealed that the quarry did not contain just the several drums visible but, rather, over one thousand drums and tanks. It readily became apparent that the quarry had been used as a dump site for containers, fluid tanks, and industrial debris. Based on these data, the EPA Superfund Removal Program, under the direction of Rose Allison and Walter Neid, conducted a massive drum removal operation utilizing commercial divers. The chemical sampling of the water in the quarry showed volatile chemicals which had the potential to penetrate some critical parts of the full face regulators being used. A safety modification was employed which involved filling a void space with cooking oil. Later the analysis of this oil showed that the chemicals did penetrate the rubber but were trapped in the oil and the divers were not exposed.

While we have concentrated on safety underwater, it should be noted that the tenders on the support vessel required not only the appropriate hazardous material training but appropriate respiratory protection. Concern was expressed that the volatile contaminants could potentially partition into the exhalation bubbles and expose the tenders on the boat. To cover this probability, air monitoring was conducted continuously on the vessel and, on several occasions the support vessel had to be moved because of potential exposure to onboard personnel. Following completion of the drum recovery operation, the ERT revisited the site to confirm the removal of all drums. The ROV was again utilized to conduct the search wherein several residual drums were located and mapped for subsequent removal.

The initial use of the ROV allowed a thorough and time critical survey of the quarry floor while preventing diver exposure to a potentially hazardous environment. Use of the ROV for the second survey allowed a rapid and cost-effective reassessment of the quarry floor.

CONCLUSION

In potentially hazardous situations, an ROV can be utilized effectively to replace divers for any direct observation task and is superior for search tasks where the target of the search could be hazardous. Benefits of ROV use include eliminating exposure potential, potential for longer-term operations, use of sonar to locate objects, and cost savings. With ROV technology, divers need not enter hazardous environments except for tasks requiring human dexterity and, as the technology improves, the use of divers may be restricted further.

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